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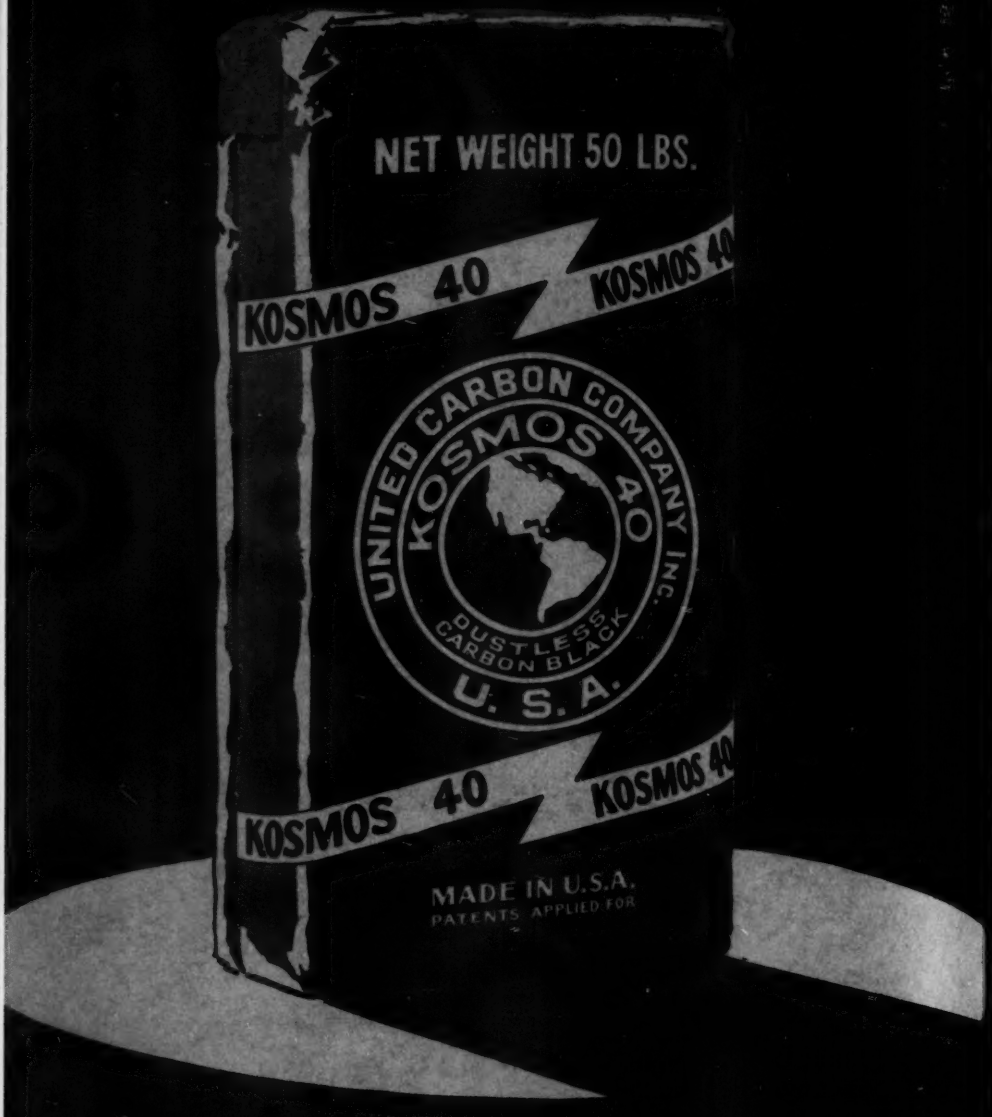
RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XX NUMBER 2

April, 1947

Published Quarterly under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY
at Prince and Lemon Sts., Lancaster, Pa.



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MODERN VIEWS ON THE CHEMISTRY OF VULCANIZATION CHANGES. I. NATURE OF THE REACTION BETWEEN SULFUR AND OLEFINS *

E. HAROLD FARMER AND F. W. SHIPLEY

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, WELWYN GARDEN CITY, ENGLAND

VULCANIZATION AND CROSS-LINKING

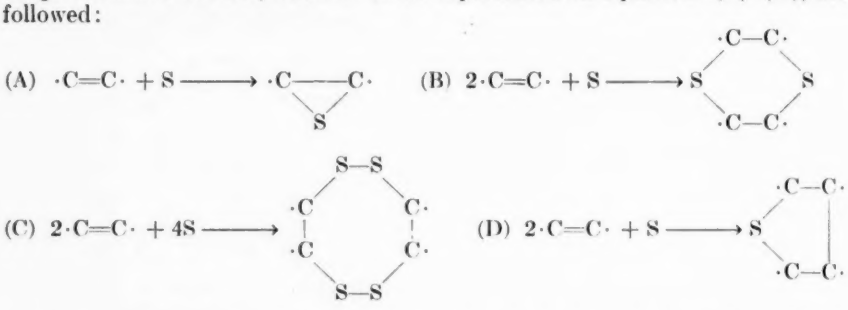
At the present time it is taken for granted that in all kinds of linear high polymers, natural or artificial, true polymers or polycondensation products, the establishment of cross-links between adjacent thread molecules is in itself sufficient to transform the physical properties of the material, producing a state which can be collated with the vulcanized state in rubber. Yet in most of these instances—and particularly in the case of vulcanization of natural and synthetic rubbers by sulfur, by peroxides, and by other reagents—the idea that the vulcanized products with their characteristic toughness, swelling capacity, elasticity, etc., derive their special qualities from the mere formation (by one means or another) of connecting links between the original linear molecules still remains a matter of hypothesis. The sulfur-vulcanization process as applied to rubber presents many interesting and very elaborate features, especially those connected with its capacity for being accelerated by a host of similar and dissimilar organic substances, and for being retarded, reversed, delicately controlled, etc. Hence, it is of considerable interest to find out by experiment exactly what sulfur does to the rubber when the two are heated together (either alone or in the presence of different types of accessory reagents) and, thence, to discover whether the production of good vulcanized properties actually depends on the production of chemical cross-links, or on certain kinds of chemical cross-links, or on a judicious combination of cross-linking and mere sulfuration (the latter possibly assisting the establishment of van der Waals forces between molecules as an auxiliary factor); or whether, as some physical chemists have been inclined to allege, it results from a state of physical association between molecules which has little or nothing to do with cross-linking. The present series of communications describes recent experimental advances in this subject; it is necessary to explain at the outset that the method of experimental approach adopted has of necessity, owing to the formidable molecular magnitude of even unvulcanized rubber, been by way of the response to vulcanization treatment of comparatively simple olefinic compounds. This approach has thus involved in the first place a study of the chemistry of simple sulfur–olefin reactivity, which was previously never carried far.

SULFUR AND THE OLEFINIC BOND

Long observation by numerous workers of the chemical character of the sulfur vulcanizates of natural rubber has resulted in the generalization that,

* Reprinted from the *Journal of Polymer Science*, Vol. 1, No. 4, pages 293–304, August 1946.

with fair exactness, one double bond of the hydrocarbon becomes saturated for each atom of sulfur which is chemically incorporated. This conclusion has rather naturally led to the assumption that the sulfur is essentially an additive reagent for double bonds, although no evidence has been adduced to show that simple additive courses, such as those represented in equations (A)–(D), are followed:



On the contrary, it is clear that there is no tradition in organic chemistry of sulfur functioning normally as an additive reagent for double bonds, as do the halogens, halogen acids, ozone, etc. It cannot be said that the methods hitherto available for measuring the unsaturation of sulfurated polyolefins are good enough to permit the true effect of sulfuration in changing the state of unsaturation of even simple molecules to be determined with exactness or certainty; the precise degree of difference between the unsaturation of rubber and that of its high-molecular and highly insoluble vulcanizates is, therefore, not reliably known. It seems very unlikely at the present stage of chemical development that any moderately simple type of sulfur–olefin additivity would not have been recognized and described, and it is perhaps not unreasonable to turn to that chemical analog of sulfur, oxygen, the high general reactivity of which toward olefinic compounds has similarly resisted correlation with any simple scheme of double-bond additivity. Oxygen has, however, in recent years been shown to react with olefinic compounds by a radical mechanism involving chain reactions, in which the first main step consists of the detachment of α-methylenic hydrogen atoms by oxygen ($\cdot CH_2 \cdot CH{:}CH \cdot + O_2 \rightarrow \cdot \overset{*}{C}H \cdot CH{:}CH \cdot + {}^*OOH$), and the second, of the addition of oxygen to the olefinic radicals so formed:

$$\cdot \overset{*}{C}H \cdot CH{:}CH \cdot + O_2 \rightarrow \cdot CH(OO^*) \cdot CH{:}CH \cdot \xrightarrow{\cdot CH_2 \cdot CH{:}CH} \cdot CH(OOH) \cdot CH{:}CH \cdot + \cdot \overset{*}{C}H \cdot CH{:}CH \cdot$$

It is quite likely that the reaction chains are started in all varieties of olefinic compounds by a few additions of oxygen molecules at one end of double bonds, but these immediately set going the detachment of α-methylenic hydrogen atoms[1].

It seemed at the outset of the work described here that sulfur, which like oxygen contains two unpaired electrons in its outer shell, might well behave in an essentially similar way to oxygen in initiating its attack on olefins ($\cdot CH_2 \cdot CH{:}CH \cdot + S_x \rightarrow \overset{*}{C}H \cdot CH{:}CH \cdot + S_xH$). If this concept is sound, it would account at once for the nonformation by sulfur of simple double-bond addition products and could probably also provide a guide to the lines of sulfur–olefin reactivity in general. The first experiments undertaken in this field

gave the strongest support to the idea of radical reaction by sulfur (probably with very short reaction chains); the succeeding experiments revealed the existence of striking relationships and differences between the action of sulfur and that of hydrogen sulfide on the same olefinic compounds.

SULFURATION OF MONOÖLEFINS

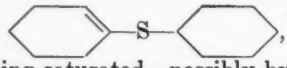
Effective attack by sulfur on olefinic compounds begins ordinarily at temperatures around the usual vulcanization temperature (140°) employed for rubber. When the two reactants are heated together at 140° for several hours, progressive, but not very rapid, reaction sets in, and there are generally produced bimolecular sulfide derivatives of the olefin, having the composition $R \cdot S_x \cdot R'$, where R and R′ are radicals derived from the olefin by loss or gain of a hydrogen atom, and x varies in magnitude from one to five according to the proportion of sulfur taken up and the duration of heating. Thus, cyclohexene, C_6H_{10}, with sulfur gives a mixture of sulfurated compounds of different boiling points and viscosities in which (*a*) the H/C ratio characterizing the original hydrocarbon survives unchanged in the sulfur compound at the value 10/6, and (*b*) the average composition of the mixture can be expressed by the formula $C_6H_9 \cdot S_x \cdot C_6H_{11}$. The last statement does not preclude the presence, to some small or large extent, of equal amounts of $C_6H_9 \cdot S_x \cdot C_6H_9$ and $C_6H_{11} \cdot S_x \cdot C_6H_{11}$ in place of the average compound, $C_6H_9 \cdot S_x \cdot C_6H_{11}$. The mixture can be separated into mono-, di-, tri-, etc., sulfides by high-vacuum (molecular) distillation, but it is highly essential that the temperature not be allowed to rise above the original vulcanization temperature, since the fractionated compounds are highly sensitive to temperatures 10° or so higher, or even to very prolonged heating at the vulcanization temperature. The higher temperatures or the prolonged heating cause severe cracking of the products, with evolution of hydrogen sulfide and thiols, and when this degradation sets in, the task of distinguishing primary from secondary products of reaction becomes impossible. In the separated mono-, di-, tri-, etc., sulfur derivatives, the average composition, $C_6H_9 \cdot S_x \cdot C_6H_{11}$, appears to be tolerably well maintained, but evidence is not lacking that, for mono-, di-, tri-, etc., sulfides, all three types of compound—$R_{sat.} \cdot S_x \cdot R'_{unsat.}$, $R_{sat.} \cdot S_x \cdot R_{sat.}$, and $R_{unsat.} \cdot S_x \cdot R_{unsat.}$—are to be found, the radical $R_{unsat.}$ containing one double bond. The question of whether those members of the polysulfide group S_x, in which $x > 2$ consist of sulfur chains or are partly coördinated assemblages of sulfur atoms, such as $\cdot S \cdot S \cdot$, is considered later.

These observations appear to preclude entirely the possibility that sulfur reacts with the olefin merely by a dehydrogenation mechanism, thereby producing hydrogen sulfide which immediately constitutes itself the effective cross-linking instrument by combining in turn with two molecules of the original olefin to give a saturated sulfide:

$$C_6H_{10} + S \longrightarrow C_6H_8 + H_2S$$

$$C_6H_{10} + H_2S \longrightarrow C_6H_{11} \cdot SH \xrightarrow{C_6H_{10}} C_6H_{11} \cdot S \cdot C_6H_{11}.$$

Jones and Reed[2] have reported that the interaction of cyclohexane and sulfur at the rather high temperature of 180° yields as main products cyclohexanethiol and dicyclohexyl sulfide, apparently formed according to these equations.

Meyer and Hohenemser[3], working at 150°, have also reported the formation of the same two products, suggesting that unsaturated compounds, SH and  , may be formed initially, these subsequently becoming saturated—possibly by taking hydrogen atoms from thiol groups; the latter correspondingly become oxidized to disulfide groups. Neither set of authors considers the significance of the accompanying high-boiling products in relation to the possibility that the saturated thiol and sulfide are purely secondary products.

If this is the actual course of reaction, there must be formed, concurrently with the hydrogen sulfide, a corresponding amount of cyclohexadiene (or more probably, benzene), whereas in practice the amount found at the end of the operation is trivial. It is true, however, that if cyclohexadiene (but not benzene) and hydrogen sulfide were indeed formed in a substantial degree, the latter might perhaps unite with the former in preference to uniting with cyclohexene; it would thereby be used up in the formation of an unsaturated thiol, $C_6H_9 \cdot SH$, which might then conceivably combine with cyclohexene to produce the average observed product, $C_6H_9 \cdot S_x \cdot C_6H_{11}$ (rather than the wholly saturated sulfide shown in the above equation) and so serve to maintain the overall H/C ratio at the value 10/6 appropriate to the original olefin. But even if hydrogen sulfide is thus generated in quantity and immediately used up in the formation of sulfides ($R \cdot S \cdot R'$), there is no likelihood that the latter could then (by secondary reaction) yield polysulfides, $R \cdot S_x \cdot R'$, the commonly obtained products of sulfuration (the amount of monosulfide in the polysulfide mixture invariably appears to be small). Experiment shows clearly that, when hydrogen sulfide is caused to react with monoölefins[4], the products, even when free sulfur is available, provided the addition is of normal type (see Part II), are monosulfides almost entirely, not polysulfides.

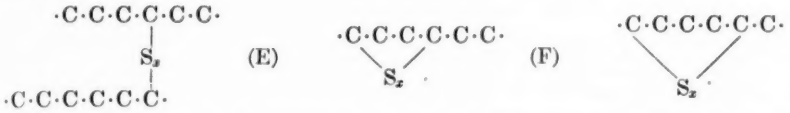
When 1-methylcyclohexene-1 (which contains the polyisoprenic unit, $\cdot CH_2 \cdot CMe{:}CH \cdot CH_2 \cdot$) is employed in place of cyclohexene, the reaction with sulfur becomes, as would be expected, easier, as is shown by the improved yields of sulfide derivatives. The products obtained, however, are strictly analogous to those from cyclohexene. There is but a mere trace of hydrogen sulfide, no recognizable yield of thiol, $R \cdot SH$, and but little monosulfide, $R \cdot S \cdot R$ or $R \cdot S \cdot R'$. The main products (as isolated by molecular distillation) are the di-, tri-, tetra-, and pentasulfides, $R \cdot S_x \cdot R'$ and (or) $R \cdot S_x \cdot R$, and the residue—as with the cyclohexene sulfuration product—consists of a quantity of highly sulfurated, undistillable substance. The experimentally determined H/C ratio of the isolated sulfides remains very close to the value, 12/7, characterizing the original hydrocarbon, thus agreeing with the average formulation, $C_7H_{13} \cdot S_x \cdot C_7H_{11}$, but not precluding the presence of equivalent amounts of $C_7H_{13} \cdot S_x \cdot C_7H_{13}$ and $C_7H_{11} \cdot S_x \cdot C_7H_{11}$.

Quite similarly the sulfuration of isobutylene at 140° gives mainly distillable products which have proved to be di-, tri-, and tetrasulfides having (an average) monoölefinic unsaturation, and agreeing in average composition with the formula, $CHMe_2 \cdot CH_2 \cdot S_x \cdot CH_2 \cdot CMe{:}CH_2$.

SULFURATION OF DIOLEFINS

In passing from a monoölefin to an isoprenic diolefin, the scope for complexity of reaction increases, because the olefin-coupling capacity characteristic

of the former can take place intramolecularly, as well as intermolecularly, with the latter. Thus a diolefin possessing the polyisoprenic ($\Delta^{1,5}$-) unsaturation pattern, $\cdot C{:}C\cdot C\cdot C\cdot C{:}C\cdot$, may reasonably be expected to give either a dimolecular sulfide, such as is shown without unsaturation details in (E), or a cyclic sulfide with a (presumably) five- or six-membered ring, as indicated in (F) and (G):



(E) (F) (G)

The formation of an episulfide (thioepoxide) containing the ring has never been reported to occur by the action of free sulfur on olefins, and no compound of this structure has been found in the present investigations.

Experiment shows clearly that the diisoprenic hydrocarbon dihydromyrcene, $CH_3\cdot CMe{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CH_3$, gives two main products. The first of these (about half the total) is a thiol-free and necessarily cyclic unsaturated monosulfide, $C_{10}H_{18}S$, which remains the original H/C ratio unchanged: this cannot then be formed by double-bond addition of hydrogen sulfide—derived by sulfur dehydrogenation of part of the hydrocarbon—to the remaining hydrocarbon, for the thiol ($C_{10}H_{19}\cdot SH$) first formed could only yield, by subsequent addition of its $\cdot SH$ group to the remaining double bond, a saturated cyclic sulfide, ($C_{10}H_{20}S$), of changed H/C ratio. The second product is a mixture of polysulfides, derived by cross-linking of dihydromyrcene molecules, and consisting largely of polysulfides, $R\cdot S_x\cdot R'$, which are strictly comparable to those derived from monoölefins. A second isoprenic diolefin, geraniolene, $CH_3\cdot CMe{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH_2$, which lacks one of the terminal methyl groups characterizing dihydromyrcene, was found to behave similarly, in that it gave with sulfur a thiol-free, cyclic monosulfide, $C_{10}H_{16}S$, as well as a roughly equal amount of an easily decomposable, high-boiling mixture of sulfides of general type $R\cdot S_x\cdot R'$.

It is obvious, of course, that cyclization in these examples is only a special (intramolecular) case of cross-linking, but if all the sulfur uptake in polyolefins occurred intramolecularly, effective vulcanization according to the cross-linking hypothesis would be impossible. Experiment shows that, in the simpler polyolefins, the amount of cyclization tends to exceed that of recognizable cross-linking.

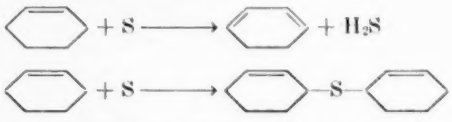
The totally undistillable material which is ordinarily obtained by sulfuration of di- and polyolefins may possibly be derived from the cross-linking of three or more molecules of hydrocarbon by sulfur, or may be partly cyclized and partly cross-linked multimolecular material. Generally speaking, however, the sulfur content of the high-boiling residues (freed as far as possible from uncombined sulfur) appears to be high.

If this condition still holds for such very high-molecular polyolefins as rubber, it becomes necessary to envisage the production by vulcanization of more sulfide rings in the carbon chains than sulfide cross-links. The quality of the vulcanizates might then be expected to vary considerably as the proportion of cyclization to cross-linking could by one device or another be induced to alter; also the scant relationship ordinarily existing between the physical properties of the vulcanizate and the total proportion of combined sulfur (which is es-

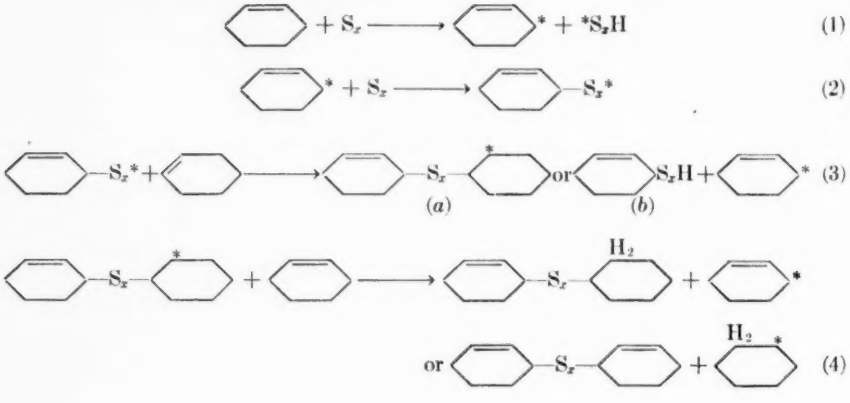
pecially noticeable when accelerated and unaccelerated vulcanizates are compared) might conceivably be the result of variation in the relative amounts of cyclization and cross-linking.

MECHANISM OF REACTION

It is necessary to recognize at the outset that the behavior of di- and polyolefins possessing the rubber unsaturation pattern, *i.e.*, possessing $\Delta^{1,5}$- and $\Delta^{1,5,9,\text{etc.}}$- unsaturation, is bound to be different in certain respects from that of olefins having other unsaturation patterns. Of the four olefinic groups to be considered, two (comprising $\Delta^{1,4}$-, $\Delta^{1,4,7,\text{etc.}}$-, and conjugated olefins) are left for future consideration. One of us suggested earlier[5] that attack by sulfur at the α-methylenic groups adjacent to double bonds probably plays an important part in sulfur–olefin chemistry in general. This means that it may be expected to play a part in sulfur vulcanization also, since the latter is likely to be a mere extension to long-chain polyolefins of the chemistry of simpler systems. Now it appears fairly certain from the foregoing results that neither a simple (Vesterburg) dehydrogenation reaction (H) followed by hydrogen sulfide addition, nor a purely α-methylenic coupling (I), represents the main result of sulfur attack on cyclohexene or 1-methylcyclohexene:

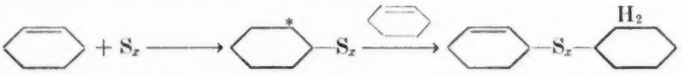


On the contrary it would appear from the fairly close maintenance of the original H/C ratio and the usual diminution in the original unsaturation that a combination of substitutive and additive functions is in question. Also, since sulfur does not show any very plain tendency to act simply as an ordinary polar reagent, but on the contrary, by reason of its compliance with certain of the criteria of radical reaction (no less than from its elemental analogy with oxygen), gives some positive indication that it enters reaction with olefinic substances by a nonpolar mechanism, one may postulate provisionally that attack by sulfur begins by displacement of α-methylenic hydrogen atoms, *i.e.*, begins substitutively, and ends additively by attachment of sulfide radical at one end of a double bond, with subsequent stabilization of the resulting radical by capture (or less usually, by loss) of a hydrogen atom, thus:



This does not necessarily mean, any more than it does for oxygen attack, that the initiation of reaction chains does not occur by addition of relatively few sulfur molecules (chain starters) at double bonds[6].

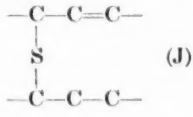
Conceivable alternative procedures are: (*a*) the addition of sulfur molecules at one end of the double bonds of two olefin molecules, with subsequent stabilization by disproportionation as shown in (5):



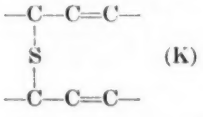
(5)

and, (*b*) the polar addition to the olefin of the thiol molecules formed by the radical mechanisms shown in (1), (2), and (3*b*) above, which would mean that the formation of sulfur rings starts as a radical reaction and ends as a polar one. Both of these alternative procedures would leave undisturbed the original H/C ratio and, on the average, reduce the original unsaturation by half; but it is clear that all three procedures could conform with the hitherto current notion regarding unsaturation loss in rubber vulcanizates (that one double bond is lost for each atom of sulfur incorporated), only provided that the cross-links in rubber vulcanizates are almost entirely monosulfide links or, alternatively, that a very high degree of homogeneous α-methylenic linking, such as is shown in (E) above (and, correspondingly little double-bond addition), is exercised in place of the substitutive-additive attack represented in reactions (1) to (5). It is particularly to be emphasized that no evidence of direct carbon-to-carbon linking of olefins (whether di-α-methylenic or substitutive-additive) has been obtained by use of sulfur. Moreover, in all those examples in which desulfuration of the sulfurated products has been successfully accomplished by the action of hydrogen adsorbed on Raney nickel (following the method of Mozingo, Wolf, Harris and Folkers[7]), only monomolecular hydrocarbons—not di- or polymolecular forms produced by cross-linking—have been obtained.

Certain recent observations have a bearing on the foregoing formulation of the sulfur–olefin reaction as proceeding partly by a di-α-methylenic coupling. The first mechanism would give rise to the characteristic allylalkyl sulfide type of grouping (J) and the second to the diallyl sulfide type (K). Thus Selker and Kemp[8] have shown that



(J)



(K)

vulcanized natural rubber reacts with methyl iodide to give crystalline trimethylsulfonium iodide in a matter which is characteristic of diallyl sulfide (and, as more recent work shows, of several other simple diallylic sulfides):

$$(CH_2{:}CH{\cdot}CH_2)_2S + CH_3I \longrightarrow (CH_2{:}CH{\cdot}CH_2)SMeI$$

$$\xrightarrow{2\ MeI} 2CH_2{:}CH{\cdot}CH_2I + Me_3SI$$

Their results suggest that much of the combined sulfur is removed from the vulcanizate by the methyl iodide treatment as if the di-α-methylenic type of cross-linking were the major one. But it is clear that if a diallylic structure such as (K), *i.e.*, a structure having both of the S−C bonds flanked by an

ethylenic center, is necessary for the production of trimethylsulfonium iodides by the scission of both S—C bonds, then a monoallylic structure such as (J) might be expected to undergo scission at only one C—S bond, leaving the sulfur attached to the carbon skeleton:

Investigation shows that the two simple sulfides of type (J), allylpropyl sulfide and cyclohexenylcyclohexyl sulfide, do not part with their sulfur in the form of trimethylsulfonium iodide by the action of methyl iodide. The matter is not quite simple, for although the experiments of Selker and Kemp[8] show definitely that much of the combined sulfur is removed from the hydrocarbon skeleton, it is not established with certainty that the sulfur so removed is all from linkages of type (K); it is also known[9] that methyl iodide is not without the ability to bring about sulfur fission even in the case of dialkyl polysulfides, and presumably, therefore, allylalkyl polysulfide. Hence the proportion of type (K) linkages is probably not so high as the experiments with methyl iodide indicate. The production of α-methylenic links to sulfur is indicated by Armstrong, Little and Doak[10] by the oxidation with ozone of the sulfides and disulfides (both considered to be of allylic type) derived by the action of sulfur on certain simple open-chain olefins. No clear evidence of any very high yield of *di*-α-methylenic linking of type (K) is provided, however, although the existence of some is demonstrated. It is of great interest in connection with the radical hypothesis of sulfuration, that the methylbutene, $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_3$, can give (owing to resonance in the allylic radical) a sulfo-grouping,—$S{\cdot}CH_2{\cdot}$-$CMe{:}CH{\cdot}CH_3$, and that its isomer, $CH_3{\cdot}CMe{:}CH{\cdot}CH_3$, can give a sulfo-grouping, $CH_2{:}CMe{\cdot}CHMe{\cdot}S$—.

Comparable with the breaking of S—C links by methyl iodide is their reductive scission by nascent hydrogen. Diallylic sulfides of type (K) undergo scission at one or both of the S—C bonds to give thiols and hydrogen sulfide (together with hydrocarbon), whereas allylalkyl sulfides of type (J) undergo scission only at the allylic S—C links to give thiol (together with hydrocarbon), but no hydrogen sulfide. Dialkyl sulfides do not reduce at the S—C bonds, but episulfides, as diallylic sulfides do, at one or both of the bonds, yielding thiol and hydrogen sulfide. It is especially significant that the cyclic sulfides derived, respectively, by the action of sulfur on dihydromyrcene and geraniolene, both undergo partial reduction to thiol, but give no hydrogen sulfide; hence it appears that groupings of type (J) are fairly abundant, but not so those of type (K).

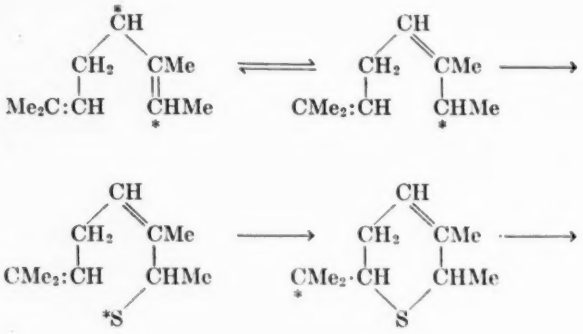
CONSIDERATIONS AFFECTING THE FORMATION OF CYCLIC SULFIDES

One of us earlier advanced the hypothesis that the production of conjugated systems from $\Delta^{1,4}$ and $\Delta^{1,4,7,\text{etc.}}$ olefins by autoöxidative action is due to the momentary production of radicals ($\cdot CH{:}CH{\cdot}\overset{*}{C}H{\cdot}CH{:}CH\cdot$, $\cdot CH{:}CH{\cdot}\overset{*}{C}H\cdot$-$CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH$, etc.) which pass by resonance into their conjugated counterparts ($\cdot CH{:}CH{\cdot}CH{:}CH{\cdot}\overset{*}{C}H\cdot$, $\cdot\overset{*}{C}H{\cdot}CH{:}CH{\cdot}CH{:}CH\cdot$, $\overset{*}{C}H{\cdot}CH{:}$-$CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH\cdot$, etc.)[11]. The same kind of resonance applies to all mono- and polyolefinic systems (including the $\Delta^{1,5}$ and $\Delta^{1,5,9,\text{etc.}}$ systems of the terpenes and rubber) from which α-methylenic hydrogen atoms have be-

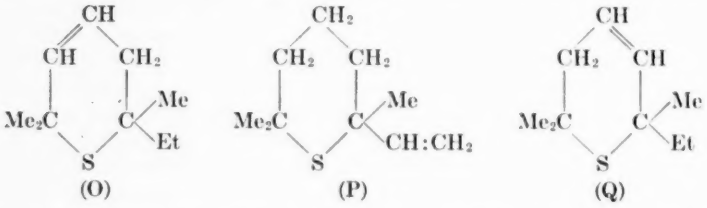
come detached in the course of oxidative, thermal, and photochemical processes. If, then, reaction by sulfur ordinarily takes place by a radical mechanism, it may reasonably be expected that double bond shifts analogous to those promoted by autoöxidation will be realized in the sulfur–olefin reaction also. In the case of the $\Delta^{1,5}$, $\Delta^{1,5,9,\text{etc.}}$ systems of polyisoprenes, the detachment of a hydrogen atom is possible at three points in each isoprenic C_5H_8 unit, although existing evidence suggests that it tends to occur at *a* in preference to *b*, and *b* in preference to *c* in $\underset{a}{CH_2}\cdot\underset{c}{C(CH_3)}:CH\cdot\underset{b}{CH_2}\cdot$. Also it must be borne in mind that most isoprenic substances of natural origin appear on good evidence to contain appreciable components in which the ordinary isoprenic unit is replaced by its isomeric (methylenic) form: $\cdot CH_2\cdot C(:CH_2)\cdot CH_2\cdot CH_2\cdot$. These complications increase considerably the number of the possible radical forms obtainable from even diisoprenic compounds such as dihydromyrcene and geraniolene, so that the prospect for the formation of a homogeneous cyclic monosulfide from either is remote—although one form may predominate in each product and certain of the others appear only in traces. There is, however, the further complication that the cyclic monosulfides consist possibly of mixtures of isomers containing 6-, 5-, and even 4-membered rings. Experimental examination of the cyclic monosulfides obtained disclosed their marked heterogeneity, and afforded slight prospect of isolating even the principal components in tolerably pure condition, or of identifying the different components by crystalline derivatives or directly by spectroscopic means. Since, however, it was unlikely that all the possible isomeric forms could be produced in any example, it was desirable to look for a simplifying factor that would restrict the number of forms to be taken into consideration. With regard to substitutive attack by sulfur (at the α-methylenic centers), the reaction possibilities are universally those given above—which cannot be further simplified; with respect to additive processes, however, a distinction may be drawn between those proceedings by a radical and those by a polar mechanism.

If for substituted ethylenes of the two types, $CRR':CH_2$ and $CRR':CHR''$(R, R′, R″ = hydrocarbon groups), it may be assumed that the polar addition of ionizable addenda of type HX, *e.g.*, $HS\cdot R$, occurs uniquely in conformity with the Markovnikov rule, whereas radical addition occurs uniquely by union of the active center at the more hydrogenated carbon atom of the ethylenic pair, *i.e.*, in the manner opposed to the Markovnikov rule, then, provided the sulfuration process has a truly radical mechanism, the number of cyclic monosulfides that can be formed is greatly reduced. There are accordingly three cases for consideration: (1) Sulfuration involves radical reaction throughout, beginning substitutively at an α-methylene group and ending additively at a double bond. (2) Sulfuration begins substitutively as a radical reaction, but each of the sulfide radicals thereby formed abstracts a hydrogen atom from the α-methylene group of a neighboring olefinic center to form a thiol ($RH \xrightarrow{-H^*} R^* \xrightarrow{S} RS^* \xrightarrow{RH} R\cdot SH$), the latter adding in polar fashion to an adjacent double bond to form a cyclic sulfide. (3) Sulfuration, in spite of the above-mentioned indications to the contrary, is wholly polar, giving first a more unsaturated (conjugated) olefin by dehydrogenation, than a thiol by addition of the liberated hydrogen sulfide to one of the double bonds, and finally a cyclic sulfide by addition of the —SH group to one of the remaining double bonds. Thus, for dihydromyrcene, if consideration is limited to the production of 6-membered cyclic sulfides, reaction according to (1) may reasonably be

expected to proceed as follows to give (L). Analogous consequences will result if cyclization leads to the formation of 5-membered sulfide rings.



By comparable attack in minor degree at other α-methylenic groups in the original olefin molecule, two other 6-membered sulfides, (M) and (N), can be formed. Similarly reaction according to (2) would be expected to yield (O) and (P), and reaction according to (3), (Q) only. Geraniolene would be ex-



pected to give cyclic sulfides differing from those obtained from dihydromyrcene only by the absence of the methyl group on the second carbon atom.

It is to be noted that the products thus expected to arise when the reaction is partly or wholly polar, as in (2) and (3), would all be identical after they had been hydrogenated, but would be different from the (single) product which would be obtained by hydrogenation of the forms (L), (M), and (N) derived by the homogeneous radical reaction. There remains, however, a further contingency to be considered, *i.e.*, the possibility that neither radical nor polar addition to double bonds is to be relied on to occur uniquely in the direction (abnormal or normal) appropriate to each in systems of the type CRR′:CHR″ and CRR′:CH_2 if departure from the rigid rule would, for purely steric reasons, considerably assist addition—and this applies particularly to cyclizing addition —in the inappropriate direction. Clearly the first necessity for narrowing the

lines of progress in the cyclizing attack by sulfur is to determine the precise course of reaction when hydrogen sulfide is caused to add to the same olefins under conditions which promote, respectively, normal and abnormal addition at the double bonds. The results of this investigation are described in Part II[4], but it can be said at once that the cyclic sulfides derived by the sulfur reaction closely resemble in certain structural features those derived by hydrogen sulfide addition, which are in the main 6-membered, *i.e.*, thiopyrane, rings.

OLEFIN POLYSULFIDES

The structure of organic polysulfides, such as those obtained above, present certain difficulties. Patrick[12] regards the tri- and tetrasulfides derived by the action of organic dihalides on sodium tetrasulfide as being basically disulfides with easily removable coordinated sulfur ($R{\cdot}S{\cdot}S{\cdot}R'$, $R{\cdot}S{\cdot}S{\cdot}R'$), and other

$$\underset{\downarrow}{S} \qquad \underset{\downarrow}{S}\,\underset{\downarrow}{S}$$

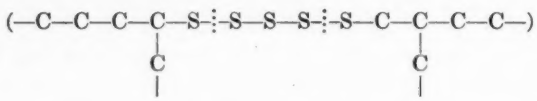
authors have supposed that analogous compounds are obtainable. Various syntheses, however, of chain polysulfides up to the penta and hexa compounds have been reported by various authors, *e.g.*, tetrasulfides from sulfur monochloride and organic metal derivatives of thiols, $2R{\cdot}SM + S_2Cl \rightarrow R{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}R + 2MCl$, and in view of the closed-chain 8-atom structure ordinarily attributed to crystalline sulfur, there is nothing improbable in the constitutions assigned. With the tri- and tetrasulfides derived by the action of sulfur on the various olefins examined, however, the extent to which combined sulfur can be removed by the action of caustic soda (the reagent used by Patrick), or sodium sulfite (the reagent used by Parker[13]), amounts only to a few units per cent of the whole. In contrast, the ethyl tetrasulfide derived by interaction of ethanethiol and sulfur monochloride, as well as that derived by interaction of sodium tetrasulfide and ethyl iodide, loses nearly half its sulfur by stripping.

An investigation of the constitution of organic polysulfides is in progress, the results of which will be reported later. For the present it is not possible to say whether, judged by the criterion of stripping liability, the sulfur in the olefin polysulfides is present wholly, or nearly so, in uncoördinated chain form. Presumably the closed chains of atoms of elementary sulfur are opened at the moment of reaction and more or less broken down into shorter chains having active radical ends. There is no special reason to suppose that these latter become rearranged (to give coördinated chains) before reacting with olefins, or otherwise unite with the olefin molecules at their own nonterminal atoms. It is clear from the fact that the cyclic sulfides formed from olefins are all monosulfides that any open chain of sulfur atoms which may become joined at one of its ends to an olefin molecule can only form a second link with the same olefin molecule to produce a cyclic monosulfide if it sheds all but one of its sulfur atoms, *i.e.*, the one linked to carbon. This presumably must mean, having regard to the nature of the electronic system concerned ($—C{=}C—C—C—C—$ $\ddot{S}{:}\ddot{S}{:}\ddot{S}{:}\ddot{S}{:}\ddot{S}{\cdot}$) and the fact that in monoölefin–sulfur reactions the polysulfide chains largely survive, that the break precedes cyclization but is not independent of it.

THERMAL DEGRADATION OF POLYSULFIDES

At temperatures above 140° the polysulfides derived from diolefins break down progressively, with formation of hydrogen sulfide, thiol, and monosulfide.

The precise course of decomposition is uncertain, but it would seem that the weakest points in the polysulfide molecules are always the S—S links:



so that mercapto radicals are formed which then give rise to thiol and cyclic sulfide molecules. The source of the hydrogen sulfide, possibly resulting from simple dehydrogenation by liberated sulfur, is as yet undetermined.

SYNOPSIS

Whatever additional factors may be concerned in the production of good vulcanizates from natural rubber by the action of sulfur, there is no doubt that the action of sulfur on olefinic substances in general at the ordinary vulcanization temperature is a chemical one, the primary course of which is determined largely by the constitution of the olefin, and hence may be profitably studied by experimentation with olefins of different unsaturation patterns. Unaccelerated reaction between sulfur and simple monoölefins leads almost exclusively to cross-linking of the separate olefin molecules, mostly in pairs, by groups of sulfur atoms. When, however, two or more olefinic units occur in the same molecule, as in the diisoprenic hydrocarbons, intramolecular cross-linking, *i.e.*, cyclization, at once becomes possible, and the results of sulfur action consists partly in the cross-linking of separate molecules as with the monoölefins, but largely in cyclization of the individual olefinic chains, thereby forming sulfur-containing rings. These changes entail a certain loss of unsaturation, from which deductions can be made as to the mechanism of the reaction.

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MODERN VIEWS ON THE CHEMISTRY OF VULCANIZATION CHANGES. II. ROLE OF HYDROGEN SULFIDE *

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INTRODUCTION

It has often been considered that hydrogen sulfide might play a considerable part in the reactions involved in the vulcanization of rubber; Fisher[1] has gone so far as to suggest that the whole process may be explained on the basis of the initial formation and subsequent reaction of hydrogen sulfide. Such a hypothesis must, however, be regarded as an oversimplification in view of the difficulty usually experienced in effecting satisfactory reaction of hydrogen sulfide with olefins. However, hydrogen sulfide is known to be liberated to some relatively small extent during the sulfur vulcanization of rubber, so that it is of interest to consider its reactivity toward olefins, particularly in the presence of sulfur. The information which has now been derived by a close study of the reactions occurring between hydrogen sulfide and mono- and polyolefins, including rubber, has led to a better understanding of the role that hydrogen sulfide may be expected to play in the vulcanization process and, what is possibly more important, to the elucidation of cyclization reactions, which are probably the reason for the relatively poor qualities of unaccelerated vulcanizates.

In the reaction of hydrogen sulfide with olefins there are two main steps to be considered: (1) the initial addition of a molecule of hydrogen sulfide to a double bond to form a thiol, and (2) the subsequent reaction of this thiol with a further double bond, resulting in the formation of a dialkyl sulfide.

$$RR'C{=}CR''R''' + H_2S \longrightarrow RR'C(SH){-}CHR''R''' \qquad (1)$$

$$RR'C(SH){-}CHR''R''' + RR'C{=}CR''R''' \longrightarrow \begin{matrix} RR'C\cdot CHR''R''' \\ | \\ S \\ | \\ RR'C{-}CHR''R''' \end{matrix} \qquad (2)$$

In each of these reactions it is theoretically possible for the hydrogen sulfide or thiol to add in one of two ways, according to which end of the double bond the mercapto group becomes attached. The type of addition which results in the hydrogen atom becoming attached to the carbon atom already carrying the greater number of hydrogen atoms, *e.g.*, $RCH{:}CH_2 + H_2S \rightarrow RCHMe\cdot SH$, is in accordance with the rule formulated by Markovnikov and is known as the normal reaction; the reverse mode of addition, *e.g.*, $RCH{:}CH_2 + H_2S \rightarrow RCH_2\cdot CH_2SH$, is termed abnormal. In the case of the very similar reaction of hydrogen bromide with olefins, the two types of addition have been explained

* Reprinted from the *Journal of Polymer Science*, Vol. 1, 4, pages 305–311, August 1946.

by assuming that the normal reaction is polar in character and the abnormal addition of a radical nature. There is evidence to indicate that a simiilar explanation is applicable to the reaction of hydrogen sulfide and thiols[2]. A study of the hyperconjugation which is intrinsic in the olefinic system, $\cdot C(CH_3):CH\cdot$, present in isoprenic compounds, shows that if in the polar reaction the initial attack is regarded as being a proton (a view that is supported by the catalytic effect of acidic compounds on the addition of hydrogen bromide and of thiols), then the addition would be expected to follow the Markovnikov rule[3].

$$H_2S \longrightarrow H^+ + SH^-$$

$$H{-}\overset{H}{\underset{H}{C}}{-}\overset{R}{C}{=}\overset{R'}{CH} + H^+ \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}\overset{R}{C^+}{-}\overset{R'}{CH_2}$$

$$H_2C{-}\overset{R}{C^+}{-}\overset{R'}{CH_2} + SH^- \longrightarrow H_3C{-}\overset{R}{\underset{SH}{C}}{-}\overset{R'}{CH_2}$$

On the other hand, in the abnormal addition, the reaction of a peroxide catalyst, or irradiation with ultraviolet light, gives rise to neutral free radicals (*Br, *SH, *SR, etc.); and it has been suggested[4] that consideration of the possibilities of resonance in the structures which would result from attack at either end of the double bond leads to the conclusion that the abnormal type of addition is energetically the more likely. The universal applicability of the argument is, however, open to some doubt.

$$*SH + R\cdot C(CH_3):CHR' \longrightarrow R\cdot\overset{*}{C}(CH_3)\cdot\underset{SH}{CHR'}$$

$$R\cdot\overset{*}{C}(CH_3)\cdot\underset{SH}{CHR} + H_2S \longrightarrow R\cdot CH(CH_3)\cdot\underset{SH}{CHR} + *SH$$

Having discussed the mechanisms underlying the two modes of reaction of hydrogen sulfide and thiols with olefins, it can now be shown how conditions of reaction influence the appearance of polar and radical addition and how this study is related to the vulcanization of rubber.

SULFUR-CATALYZED REACTION OF HYDROGEN SULFIDE WITH OLEFINS

Monoölefins.—Jones and Reid[5] first reported that the reaction of hydrogen sulfide with olefins was positively catalyzed by elementary sulfur, and that the mode of addition was in accordance with Markovnikov's rule. However, the relatively large quantities of catalyst used in some of these experiments introduced a measure of uncertainty as to what extent the products had arisen by reaction of the hydrogen sulfide and to what extent by reaction of the sulfuric catalyst with the olefins. Further examinations of the reaction of hydrogen sulfide with representative monoölefins, *e.g.*, with isobutylene and cyclohexene, have shown definitely that not only does sulfur catalyze the addition, but also

that quite small amounts of sulfur are sufficient to promote a considerable degree of reaction at 140° C. The main products in each case are the thiol and a monosulfide that is formed by sulfur-catalyzed addition of a molecule of the thiol to a further olefin molecule. In the case of isobutylene the products are quite definitely tertiary butyl derivatives arising by normal addition:

$$CMe_2{:}CH_2 + H_2S \longrightarrow CMe_2(SH)\cdot CH_3$$
$$CMe_2{:}CH_2 + CMe_2(SH)\cdot CH_3 \longrightarrow CH_3\cdot CMe_2\cdot S\cdot CMe_2\cdot CH_3$$

but with cyclohexene, owing to its symmetry, no differentiation between the products of normal and abnormal addition is, of course, possible. It is of considerable interest that a small amount of disulfide accompanies the other reaction products and that it arises even when air is excluded and in experiments where no sulfur is included (the reaction being then catalyzed to a small extent by the iron sulfide formed on the walls of the steel autoclave used in the experiments). As atmospheric oxidation of the initially formed thiol is excluded, it would appear that the oxidation must be associated with a complementary reduction, *i.e.*, hydrogenation of the olefin[6].

Polyisoprenes.—The presence of the $\Delta^{1\cdot5}$-diene system in polyisoprenic compounds adds considerably to the inherent possibilities of reaction with hydrogen sulfide. If the diisoprene, dihydromyrcene, is considered as a typical compound of this group ($CH_3CMe{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe$), it is found that, initially, one molecule of hydrogen sulfide adds normally to one or the other of the double bonds to give a monothiol. Four courses of reaction now remain open:

(1) A second molecule of hydrogen sulfide may add to the thiol giving a dithiol:

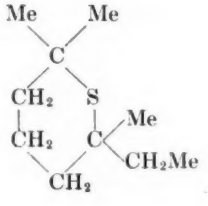
$$Me_2C{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe \longrightarrow$$
$$Me_2C(SH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe \longrightarrow$$
$$Me_2C(SH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot C(SH)Me\cdot CH_2Me$$

(2) The monothiol may add to a second molecule of dihydromyrcene or to the second double bond of a further molecule of monothiol to give a monosulfide or mercaptosulfide, which contains four C_5 units:

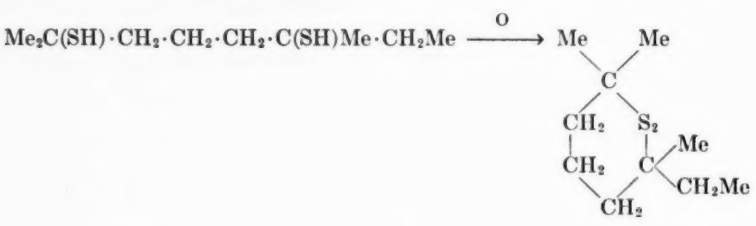
$$Me_2C(SH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe \quad + \quad Me_2C{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe \longrightarrow Me_2C(S\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe)_2$$

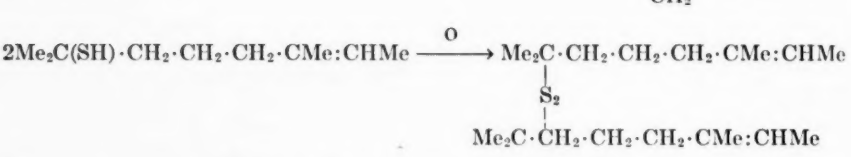
(3) The mercapto group may add in an intramolecular manner, *i.e.*, to the other double bond in the same molecule, giving a cyclic sulfide, containing a 6-membered ring:

$$Me_2C(SH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe \longrightarrow$$

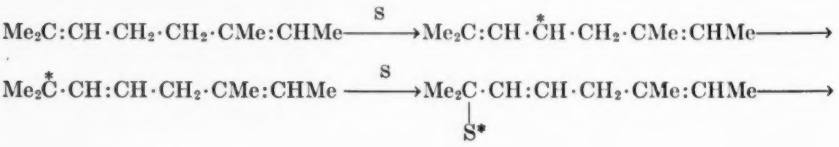


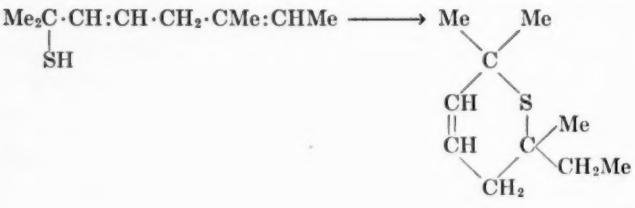
(4) Two mercapto groups, in the same or different molecules, may be oxidized (see above) to form a disulfide:





In actual practice, with both dihydromyrcene and geraniolene, it is found that by far the most important reaction is (3). Reactions (1) and (4) take place to a negligible extent, and reaction (2) occurs to give a very small yield of cross-linked sulfides. The importance of these observations in relation to the vulcanization of rubber is obvious, as it means that if such reactions play any considerable part in the vulcanization process, then, in the absence of adventitious materials, *e.g.*, zinc oxide, accelerators, a very high percentage of the total sulfur goes to form cyclizing links, which are valueless from the point of view of strengthening the molecular network of rubber. In this connection it is significant that, as far as present evidence goes, the cyclic products formed by reaction of sulfur with dihydromyrcene and geraniolene[7] show a greater resemblance to the cyclic sulfides derived by polar, *i.e.*, sulfur-catalyzed, addition of hydrogen sulfide to these olefins than they do to those obtained by radical (ultraviolet light-catalyzed) addition (see below) of hydrogen sulfide. This may possibly be explained—as indicated among the possibilities of sulfur reaction in Part I[8]—by assuming that the mercapto radical formed by sulfur attack preferentially captures a hydrogen atom to become a thiol of the same structure (apart from the incidence of unsaturation) as that obtained by polar addition of hydrogen sulfide; under the influence of sulfur this mercaptan adds normally in an intramolecular manner:





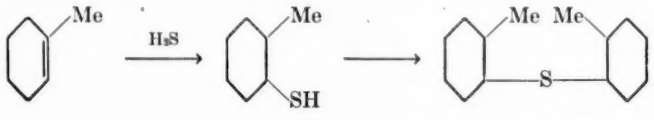
Such a hypothesis is consistent with the observed fact that addition of the monothiol is very effectively catalyzed by sulfur. In the sulfur-catalyzed reaction of hydrogen sulfide with polyisoprenes, monothiol and cyclic sulfide are formed in approximately the ratio of 1:8. When the reactions are repeated using aluminum sulfide instead of sulfur as a catalyst, although the overall yields are not much reduced, this ratio is reduced to 1:2 or sometimes nearly 1:1. In addition some dithiol is formed, according to reaction (1) above, indicating that the speed of addition of hydrogen sulfide is now of the same order as that of the thiol.

Rubber.—The high molecular weight of rubber renders impossible the separation and identification of individual reaction products in the manner that is feasible with simpler olefins. However, it has been shown that solid rubber does react with hydrogen sulfide under pressure at 140° C in the presence of either sulfur or iron sulfide; the properties of the products indicate that some sulfide cross-links are being formed. Dissolution of hydrogen sulfide in the rubber during the reaction gives rise to bubbles in the sheet when pressure is released, with the result that it is very difficult to obtain samples of the product which are suitable for tensile strength tests. Nevertheless, selected portions of products containing 2–3 per cent of combined sulfur are capable of over 700 per cent elongation. Although the reaction of diisoprenes with hydrogen sulfide indicates an overwhelming preponderance of intramolecular over intermolecular addition, it is probable that this is offset to some extent in the case of rubber by the purely physical intermolecular entanglements of the long rubber molecules.

ULTRAVIOLET LIGHT-CATALYZED REACTION OF HYDROGEN SULFIDE WITH OLEFINS

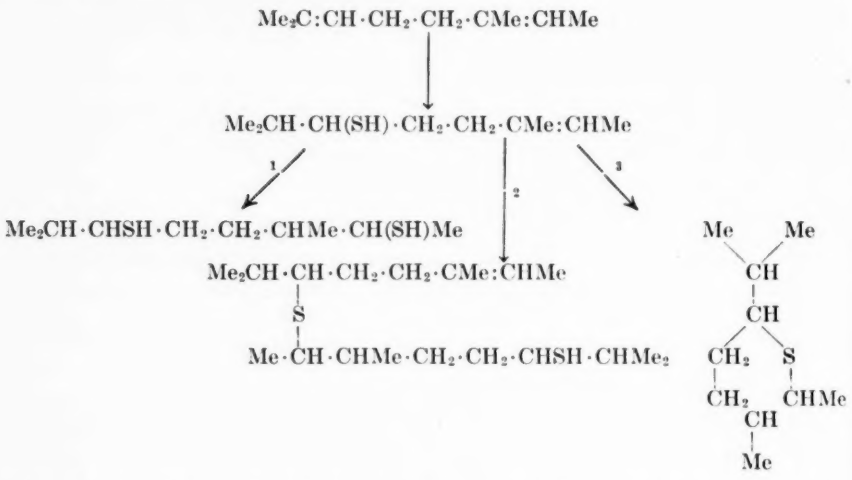
It has been shown by Vaughan and Rust[9] that hydrogen sulfide becomes dissociated on irradiation by ultraviolet light and that the resulting mercapto radicals attack olefins to give the abnormal products. As it is considered[8] that the reaction of sulfur with olefins under vulcanization conditions is, in the initial stages at least, a radical reaction, it is of interest to study the radical addition of hydrogen sulfide to olefins.

Irradiation of mixtures of liquid hydrogen sulfide with such simple olefins as 1-methylcyclohexene, the latter containing the isoprenic unit, $-C(CH_3):CH-$, results in the formation of the corresponding alkyl thiol and dialkyl sulfide by abnormal addition.



The diisoprene, dihydromyrcene, reacts similarly with the formation of a monothiol, which then follows the reaction schemes (1), (2), and (3) for polyisoprenes enumerated in the section dealing with the sulfur-catalyzed reaction[10]. In this case it is found that about 50 per cent of the monothiol remains as such, while most of the remainder reacts intramolecularly to give a cyclic sulfide; small amounts of dithiol and of intermolecular sulfides are also formed. The persistence of much of the monothiol under conditions that are eminently suited to radical reaction lends support to the hypothesis that in the reaction of sulfur

with polyisoprenes, the radical chain mechanism proceeds, in the main, only as far as the thiols and the subsequent addition reaction is of a polar type. It will be noted that the abnormal reaction gives rise to products which are different from those obtained in the sulfur-catalyzed normal reaction and, although the cyclic sulfide obtained again contains a 6-membered ring, the substituents in the ring are now differently oriented.



It is thus possible to distinguish between products resulting from a radical addition and those from a polar addition of hydrogen sulfide and this comparison has been of value in examination of the cyclic sulfides arising by sulfur attack on polyisoprenes (see above).

Under the influence of ultraviolet irradiation, rubber itself reacts with hydrogen sulfide, either when its solution in a hydrocarbon solvent is saturated with the gaseous reagent, or when it is dissolved directly in liquid hydrogen sulfide (in which it is reasonably soluble). Although precise elucidation of the mode of reaction is not possible with the complicated rubber molecule, the nature of the products obtained does indicate that some of the sulfur atoms are utilized in forming cross-links of the same types as have been identified in the work with simpler compounds.

CONCLUSIONS

1. The normal addition of hydrogen sulfide to olefins is catalyzed by very small proportions of sulfur, but the rate of addition is too slow to provide a satisfactory basis for the hydrogen sulfide-actuated mechanism of vulcanization.

2. The main products of the sulfur-catalyzed (polar) reaction of hydrogen sulfide with polyisoprenes are substituted pentamethylene sulfides, derived by intramolecular normal addition of the initially formed monothiols.

3. The main products of the ultraviolet light-catalyzed (radical) reaction of hydrogen sulfide with polyisoprenes are monothiols and substituted pentamethylene sulfides, the latter derived by intramolecular abnormal addition.

4. The resemblance of the cyclic sulfides obtained by reaction of free sulfur with polyisoprenes to the products of polar hydrogen sulfide addition (as opposed to the products of the radical-type addition) supports the hypothesis

that, in the sulfur–olefin reaction, the radical reaction chain is terminated by the capture of a hydrogen atom by an RS* radical, the thiol so formed adding intramolecularly in a polar reaction catalyzed by sulfur.

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MODERN VIEWS ON THE CHEMISTRY OF VULCANIZATION CHANGES. III. REACTION OF SULFUR WITH SQUALENE AND WITH RUBBER *

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INTRODUCTION

The hexaisoprene, squalene ($C_{30}H_{50}$), is a promising hydrocarbon for inclusion in a comprehensive survey of sulfur–olefin reactivity and the mechanism of rubber vulcanization, since its molecular complexity is such as to render it more closely comparable with long-chain polyisoprenes than is the diisoprene dihydromyrcene, while its molecular weight is still sufficiently low to enable molecular distillation of the sulfurated reaction product to be accomplished without recourse to unduly elevated temperatures. It has been shown elsewhere[1] that the behavior of squalene toward halogens resembles more closely that of rubber than does the behavior of dihydromyrcene. It is now found that the reaction of squalene with sulfur at the ordinary vulcanization temperature pursues a course very similar to that of dihydromyrcene[2] while at the same time showing a close resemblance to rubber–sulfur vulcanization.

REACTION OF SQUALENE WITH SULFUR

When squalene and sulfur were heated together at 140°, both monomolecular and bimolecular sulfurated products were formed, which were readily separable by molecular distillation. In neither portion of the reaction product was there any overall change in the ratio of hydrogen to carbon from that of the original hydrocarbon. In the monomolecular product, olefinic unsaturation had been destroyed in the proportion of one double bond per sulfur atom incorporated, but no mercapto groups were present; by analogy with dihydromyrcene it may reasonably be considered to be a cyclic sulfide. (A precise method for determining the olefinic unsaturation of soluble substances of low sulfur content has recently been described[3].) The bimolecular product appeared to be a polysulfide of the overall composition $C_{60}H_{100}S_6$. Of the squalene which entered into reaction with sulfur $\lessapprox$24 per cent formed monomolecular cyclic sulfide and $\gtrapprox$10 per cent formed bimolecular polysulfide. Of the sulfur originally present, 37 per cent entered into reaction, and of this at least one-half formed the monomolecular product. The presence of mercaptobenzothiazole and zinc oxide during the reaction of squalene with sulfur increased the yields of both products, but did not raise the proportion of the intermolecularly linked product at the expense of the intramolecular sulfide. An increase in the proportion of monosulfide at the expense of polysulfide has been reported with this accelerator in the reaction of sulfur with 2-methylbutene[4].

* Reprinted from the *Journal of Polymer Science*, Vol. 1, No. 4, pages 312–317, August 1946.

RUBBER VULCANIZATION

The chief characteristics of the vulcanization of rubber with sulfur are: first, that there is no overall loss of hydrogen relative to carbon in vulcanizates containing considerable proportions of combined sulfur, and, second, that there is a loss of unsaturation accompanying sulfur combination corresponding to one double bond per sulfur atom incorporated[2]; if zinc oxide or certain mixtures of zinc salts and accelerators are present the loss of unsaturation may be substantially less.

FORMATION OF HYDROGEN SULFIDE AND ITS INFLUENCE ON THE REACTION OF SULFUR WITH RUBBER

Small amounts of free hydrogen sulfide (containing a total of sulfur equivalent to 1–2 per cent of that entering into combination with the rubber) can be detected during vulcanization even when the purest available fractionated rubber hydrocarbon (N < 0.01 per cent) is used. Hydrogen sulfide has, moreover (as already observed by Buizov and Popova[5]), a marked catalytic effect on rubber–sulfur combination, promoting combination of a proportion of sulfur considerably in excess of that which would be obtained even if all of the hydrogen sulfide present were added to the rubber. Experiment showed, however, that in the presence of the considerable proportion of sulfur normally used in vulcanization processes, the amount of combined sulfur resulting from combination of hydrogen sulfide was not large, and over a fairly wide range of relative concentrations of rubber, sulfur, and hydrogen sulfide the following relationship was maintained:

$$\frac{\text{combined S contributed by } H_2S}{\text{combined S contributed by free S}} = \frac{\text{S present as } H_2S}{\text{S present as free S}}$$

This relationship indicated that addition of hydrogen sulfide to rubber might become appreciable if the amount of hydrogen sulfide present was greatly increased while the amount of sulfur present was suitably reduced; this has indeed been found to be so. Moreover, the sulfur content arising from the combined hydrogen sulfide then made a significant contribution to the physical properties of the resulting vulcanizate.

As might be expected from the foregoing considerations, the reaction between purified rubber and sulfur in a sealed evacuated tube is appreciably autocatalytic, contrary to the well established linear rate of combination of sulfur with rubber observed in technical vulcanization. This difference in behavior can probably be attributed to oxygen, which is found to suppress appreciably the catalytic activity of hydrogen sulfide.

Ethanethiol has a catalytic effect on rubber–sulfur combination comparable to that of hydrogen sulfide, but diethyl sulfide is entirely without effect. Diethyl disulfide slightly increases the sulfur content of a vulcanizate of which it is an ingredient, but the increase does not contribute to the physical properties of the vulcanizate and probably arises partially from combination of the disulfide itself with the rubber (see below).

Accelerated vulcanization exhibits rather different characteristics, since the rate of combination of sulfur decreases rapidly with time and the catalytic effect of hydrogen sulfide may be very much reduced or entirely absent according to the type of accelerator used.

When nonaccelerated vulcanization is conducted with rigid exclusion of oxygen, slightly higher sulfur contents are obtained in comparison with vul-

canization conducted in the presence of quite limited amounts of oxygen, and there is a corresponding improvement in the physical properties of the vulcanizate. It cannot be stated with certainty, however, whether this effect is due to an inhibition of rubber–sulfur combination (as suggested by Armstrong, Little and Doak[4]) or to an inhibition of the autocatalytic effect of hydrogen sulfide.

NATURE OF THE SULFUR LINKAGE IN VULCANIZED RUBBER

The formation of trimethylsulfonium iodide from vulcanized rubber and methyl iodide[6] can be accepted as a rigid proof of the presence of di-α-methylenic linkages only if alkylalkenyl sulfides, polysulfides, and the cyclic sulfides formed from dihydromyrcene and squalene do not form trimethylsulfonium iodide with methyl iodide. In the investigation described[7] in Part I, no evidence of trimethylsulfonium iodide formation from any of these compounds has been found; it must accordingly be accepted that some part of the sulfur in vulcanized rubber is present in di-α-methylenic linkages. Since there is no overall reduction in the ratio of hydrogen to carbon, and since unsaturation is lost during vulcanization, it necessarily follows that there must be present a proportion of the fully saturated sulfur-linked compound, R—Sx—R′, equivalent to the amount of di-α-methylenic sulfur linked component, R $|^{-}{}_{1}$—S_x—R′.

The formation of a cyclic sulfide instead of an intermolecularly linked monosulfide appears to be common to both dihydromyrcene and squalene; with rubber the extensive formation of cyclic sulfides may perhaps be rendered more difficult by the lower order of mobility in the rubber system, in which cross-linking is simultaneously occurring by intermolecular reaction.

Polysulfide Formation in Rubber.—Treatment of vulcanized rubber with aqueous solutions of sodium sulfite reveals the presence of a very small proportion of polysulfide sulfur, but the actual amount present may well be considerably in excess of that indicated, since a low order of reactivity toward sodium sulfite is shown by some of the higher polysulfides, *e.g.*, Thiokols and the squalene polysulfide described above; even dicyclohexyl tetrasulfide is fairly stable toward this reagent.

Structure of the Polysulfides.—No great differences have been observed in boiling point, refractive index, and reactivity of samples of dialkyl tetrasulfides prepared, respectively, from alkyl halides and sodium tetrasulfide and from thiols and sulfur monochloride. Since sodium sulfite readily removes two atomic proportions of sulfur from samples of diethyl tetrasulfide prepared by either method, it follows that this reagent can abstract sulfur atoms from a linear chain because—whatever the structure assigned to sulfur monochloride—three of the sulfur atoms of the corresponding tetrasulfide must be in a linear chain. But, since Palmer[8] has obtained evidence which favors the wholly linear structure, Cl·S·S·Cl, for sulfur monochloride, a wholly linear structure, R·S·S·S·S·R, for the tetrasulfides seems highly probable. Hence it cannot be assumed that ability to yield up sulfur to sodium sulfite or caustic alkali is evidence of the presence of coördinated sulfur atoms.

Thermal Stability of Polysulfides.—The intermolecular linked squalene polysulfide underwent appreciable loss of unsaturation, accompanied by a small increase in thiol content, on being heated to 160–180°, although the overall composition was not appreciably changed. This behavior is not altogether surprising, since tetrasulfides have been shown to react fairly readily with olefins[9] at temperatures exceeding 140°. Even disulfides undergo thermal dissociation into RS* radicals[10].

In the determination of the unsaturation of vulcanized rubber a necessgry prerequisite is to bring the sample into solution by heating it to 160–180° with a nonvolatile solvent, during which treatment there is a high probability of breakdown of polysulfide linkages, with a corresponding reduction of unsaturation of the rubber. The ultimate finding, after dissolution, of an average loss of unsaturation amounting to one double bond per sulfur atom is not, therefore, inconsistent with the presence of polysulfide linkages which would normally require a loss of unsaturation of $|^{-}_{0}$, $|^{-}_{1}$, or $|^{-}_{2}$ per x sulfur atoms in dialkenyl, alkylalkenyl, or dialkyl polysulfides, respectively. It is noteworthy that the bimolecular squalene polysulfide exhibits a considerably smaller loss of unsaturation than that corresponding to $|^{-}_{1}$ per sulfur atom unless it is given severe heat treatment comparable with that prescribed for a vulcanized rubber. The small decrease in unsaturation on overcure of some accelerated vulcanizates (notably when accelerated by zinc dimethyldithiocarbamate) reported by Brown and Hauser[11] appears to be a result of oxidation, since an identical experiment conducted with rigid exclusion of air showed no change in unsaturation on overcure. There is good ground for believing that the necessity for heating the vulcanizates before determining their unsaturation is in itself sufficient to obscure any real change in unsaturation produced by sulfur redistribution.

On heating a polysulfide and an olefin together, three types of reactivity of the polysulfide have been observed: (1) Some disulfides gave small proportions of the corresponding thiols, probably by a radical mechanism:

$$R_2S_2 \longrightarrow 2RS^{\bullet} \xrightarrow{R'H} RSH + \overset{\bullet}{R}'$$

(2) Tetrasulfides and some disulfides gave evidence of the occurrence of partial addition to the olefin of radicals resulting from fission of —S—S— linkages, but part of the sulfur liberated from the tetrasulfide also reacted with other olefinic linkages. Throdahl and Beaver[12] observed that alkyl tetrasulfides do not vulcanize rubber in a physical sense, but they did not report any tendency for nonvulcanizing combinations of either liberated sulfur or liberated sulfurated fragments to occur with the rubber. On the other hand, the known rubber-vulcanizing properties of some long-chain polysulfides[13] of the type —R—S_x—R—S_x— may be due to attachment of polyfunctional long-chain dissociation fragments to unsaturated centers in the rubber. (3) Tetramethylthiuram disulfide gives evidence of both thiol formation[14]:

$$(CH_3)_2N{-}\overset{\overset{S}{\|}}{C}{-}S{-}S{-}\overset{\overset{S}{\|}}{C}N(CH_3)_2 \xrightarrow[S,\ ZnO]{\text{olefin}} (CH_3)_2N\overset{\overset{S}{\|}}{C}{-}S{-}Zn{-}S{-}\overset{\overset{S}{\|}}{C}N(CH_3)_2$$

and radical dissociation, the latter process yielding sulfur, thiourea, and carbon disulfide. It is noteworthy that the yield of carbon disulfide amounts to 40 per cent of the theoretical in the presence, and 70 per cent in the absence, of zinc oxide.

ROLE OF ZINC OXIDE IN VULCANIZATION

The addition of zinc oxide to rubber and sulfur does not increase the rate of combination of sulfur with the rubber, but does substantially increase the rate of physical cure. Various workers have suggested that additional cross-linking is brought about by formation of a metal derivative of a thiol or by the subsequent action of sulfur on a metal derivative of a thiol[3]. The sulfur–zinc

oxide combination, however, reacts readily with thiols in a manner quite different from the action of sulfur on metal derivatives of thiols, as expressed by the equation:

$$R{\cdot}S{-}Zn{-}S{\cdot}R \xrightarrow{S} R{\cdot}S{\cdot}S{\cdot}R + ZnS$$

Indeed, at temperatures above 70° a reaction occurs which involves liberation of hydrogen sulfide but not any significant degree of formation of zinc sulfide:

$$2RSH + S \xrightarrow{ZnO} RS_xR + H_2S$$

The zinc oxide functions mainly as a catalyst, and only a small proportion is required; zinc stearate is almost equally effective. Polysulfides are readily formed in the presence of an excess of sulfur, but with smaller amounts of sulfur a disulfide is the major product. The corresponding reaction of thiols with sulfur alone is extremely slow, even at 140°.

Many accelerators of rubber vulcanization show the same type of reaction-promoting activity toward thiol and sulfur as does zinc oxide, but they are considerably more effective than the latter, and polysulfides are readily formed even at room temperature. The nitrogenous basic accelerators piperidine, piperidiniumpentamethylene dithiocarbamate, diphenylguanidine, and butyraldehydeaniline, are the most reactive and tetramethylthiuram disulfide is somewhat less reactive; zinc dimethyldithiocarbamate shows considerable activity at 70° doubtless due to its relationship with tetramethylthiuram disulfide but in general the disulfide accelerators and the corresponding thiol accelerators are relatively ineffective.

When rubber, sulfur, and either cyclohexane thiol or ethane thiol were heated together at 140° at least 50 per cent of the thiol was converted to isolable disulfides and polysulfides in the course of an hour; the reaction of the thiol with the sulfur did not in this instance necessarily require the presence of either zinc oxide or an organic accelerator, although in their absence di- and polysulfides did not proceed quite so readily. In none of these experiments was more than a trace of hydrogen sulfide liberated; consequently the hydrogen sulfide resulting from the thiol oxidation must have entered into immediate reaction with the vulcanizing rubber, possibly by a radical mechanism. The formation of no more than trace quantities of hydrogen sulfide during ordinary vulcanization processes is no proof of the absence of reactions involving the conversion of mercapto groups to di- and polysulfides; it therefore appears certain that if any mercapto groups are formed in the course of vulcanization reactions, a considerable proportion of them may be expected to undergo conversion into di- and polysulfide intermolecular linkages.

SYNOPSIS

Squalene containing six isoprene units is more nearly free of end-group effects and less limited in the range of space-distributional contortions of its carbon chain than mono- and diolefins. Hence it is more comparable with rubber than the latter group where matters of chemical reactivity are concerned. Nevertheless, in its reaction with sulfur, squalene pursues a course very similar to that followed by the diisoprene, dihydromyrcene, in that intramolecular sulfide linkages as well as intermolecular polysulfide linkages are formed. Taking into consideration the amount of sulfur which would suffice for the establish-

ment of some given number of the simplest possible intermolecular linkages, *i.e.*, monosulfide linkages, the efficiency of sulfur as a cross-linking reagent during the vulcanization of squalene is seen to be of a rather low order; this condition might be expected to hold for rubber in the absence of auxiliary mechanisms. So far as can be determined by direct experiment the action of sulfur in forming cross-links is not essentially different from that encountered with squalene, since there are indications that both intra- and intermolecular sulfide linkages are formed—the latter being of both dialkenyl and dialkyl sulfide type, and, possibly also of alkenylalkyl type. Under the influence of small amounts of zinc oxide or of various nitrogen-containing organic accelerators, sulfur reacts with the thiol groups of organic thiols, forming di- and polysulfides, together with hydrogen sulfide. In the presence of rubber the same reaction occurs without actual liberation of hydrogen sulfide and it thus appears that if any thiol groups are formed as intermediates in vulcanization they will undergo ready conversion into intermolecular di- and polysulfide linkages. This may well represent an important auxiliary mechanism of cross-linking.

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PEROXIDATION IN RELATION TO OLEFINIC STRUCTURE *

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PEROXIDATION AND PEROXIDE BREAKDOWN

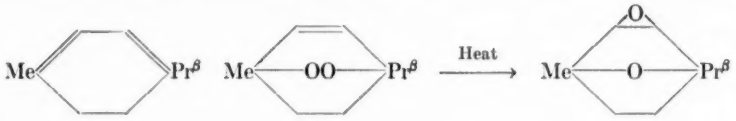
The process of autoxidation among olefinic substances comprises two major phenomena, that of the incorporation of molecules of oxygen (peroxidation), and that of secondary change (peroxide breakdown) during which the peroxide groups formed by this incorporation act as oxidizing agents for adjacent unsaturated centers. Interest may, accordingly, be directed towards two quite distinct but composite themes, *viz.*: (1) the nature of the mechanism by which the oxygen molecules are incorporated, the positions they take up in different kinds of organic molecules, and the effect of their introduction in causing (or not causing) specific types of molecule-linking, and (2) the inherent stability or instability of the peroxide groups in different molecules and its structural cause, the mechanism of breakdown of the peroxidic groups and the way this is influenced by light, heat, or catalytic influences, and finally the manner of utilization of the "active" oxygen given up by the decomposing peroxide groups in forming (by inter- or intramolecular reaction) new oxygeno-groups or, alternatively, in bringing about some small or large degree of scission of the carbon chains. Wherever the peroxido-olefins have a moderately high degree of stability, and they are consequently isolable in tolerably pure condition, no serious difficulty attends the systematic study of their thermal, photo-, or catalyzed decomposition, although as yet but little systematic work has been done in this field: but where their degree of unstability is very high, deductions concerning the character of the peroxido-olefinic structures produced and of their breakdown mechanisms have to be made (at any rate in the first place) from the nature of the secondary autoxidation products actually isolated in practice, and there is then grave danger of erroneous conclusions being drawn. Of course, many autoxidation products are extremely complex in character, and where this is the case the difficulty of correlating breakdown products with their peroxidic precursors is greatly increased. Therefore in prosecuting autoxidation studies, especially those directed towards determining the mechanism of reaction, it is very desirable to have as general guide a detailed knowledge of the structure and breakdown behavior of all the various distinctive types of organic peroxide which are capable of existence, and the following survey represents in the main a contribution in this direction.

PEROXIDES OF HIGH STABILITY

All peroxides of non-aromatic conjugated dienes and polyenes so far examined, whether these are open-chain or cyclic, formed rapidly in ultraviolet light or slowly in diffused light, are known to be produced by addition of oxygen

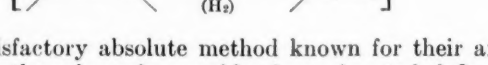
* Reprinted from the *Transactions of the Faraday Society*, Vol. 42, Parts 3–4, pages 228–236, March–April 1946.

at the terminals of the diene systems. Even if the conjugated system is flanked on one or both sides by $\cdot CH_2\cdot$ groups, *e.g.*, as in sorbic ester[1], CHMe:CH·-CH:CH·CO_2Me, and elaeosteric ester[2], $C_4H_9\cdot[CH:CH]_3\cdot[CH_2]_7\cdot CO_2Me$, the reaction is still restricted to addition at the double bond system. The peroxide of α-terpinene (I), which occurs naturally in chenopodium oil, is a monomeric compound (II), sufficiently stable to be distilled at 10–15 mm. pressure[3], but all investigated artificially-formed peroxides of conjugated ole-



(I) (II) (III)

finic compounds, although these also show high thermal stability[4], are polymeric substances (apparently polymer-homologs) which probably rarely exceed octameric complexity, and normally contain little or no monomeric component. Not only do these monomeric and polymeric peroxides show high thermal stability, but they undergo so incompletely chemical reduction and catalytic hydrogenation—which might perhaps be expected to sever quantitatively the $\cdot OO\cdot$ pairs:



that there is no satisfactory absolute method known for their analytical determination. If now the polymeric peroxide of a conjugated olefin, CHR:CH·-CH:CHR′, has the constitution of a polymeric 1,4-adduct or interpolymer, and this is the most reasonable view, it must in fact be a stabilized form of the

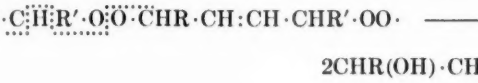
(A) *CHR·CH:CH·CHR′·OO·[CHR·CH:CH·CHR′·OO]$_n$
·CHR·CH:CH·CHR′·OO*

(B) *OO·CHR·CH:CH·CHR′·OO[CHR·CH:CH·CHR′·OO]$_n$
·CHR·CH:CH·CHR′·OO*

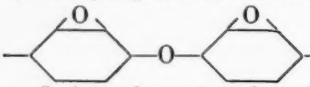
diradical (A) or (B), in which stabilization of the free ends is probably achieved by loss or gain of H atoms (perhaps by disproportionation between pairs of molecules) or, alternatively, by direct union of the two end groups of each polymer of type (A). It is impossible by ordinary elementary analysis to distinguish in polymer-homolog mixtures between the peroxide forms (C),

(C) ·C:C·C:C·OO·[C·C:C·C·OO]$_n$·C·C:C·C·OOH
(D) C·C:C·C·OO·[C·C:C·C·OO]$_n$·C·C:C·C·OO
(E) HOO·C·C:C·C·OO·[C·C:C·C·OO]$_n$·C·C:C·C·OOH

(D) and (E), although some idea of the prevalence of forms (C) and (E) might doubtless be gained from active hydrogen determinations. Catalytic hydrogenation, however, fails to give a quantitative reduction to the monomeric 1,4-diol, because the metal surface promotes extensive catalyzed decomposition in the sense:



to give 1,4-ketols. Thus the polymeric peroxide of elaeostearic ester gives at least a 60 per cent yield of mixed hydroxyketo- and dihydroxystearic esters.[2] Polymeric cyclohexadiene peroxide gives by catalytic hydrogenation both *cis* and *trans*-1,4-dihydroxy-cyclohexene and polymeric α-terpinene peroxide on half-hydrogenation a corresponding 1,4-dihydroxymenthene, but in neither case has the corresponding 1,4-ketol yet been recognized[5]. Ascaridol undergoes hydrogenation to give moderate yields of the 1,4-diol, but when it is heated in an inert solvent it is extensively and nonexplosively transformed into the ether-epoxide (III)[3]. Whether the latter change is intra- or intermolecular is uncertain, but the thermal decomposition of ascaridol in presence of cyclohexene has failed to give a recognizable amount of cyclohexene epoxide[1]. It is possible that the ascaridol type of peroxide transformation also occurs in the catalytic hydrogenation of the polymeric peroxides of cyclic dienes, since nonhydrogenatable polymeric products often accompany the scission products; it seems, however, improbable that homogeneously constituted polymeric ether-epoxides



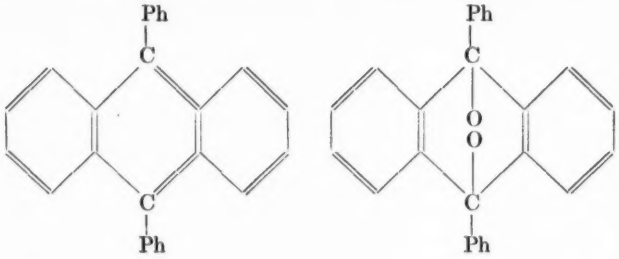
could ever be formed.

It is to be noted that the crude polymeric peroxides formed from open-chained conjugated systems contain usually a proportion of oxidative scission products (up to 20 per cent), and these may either be formed wholly spontaneously and unavoidably during the absorption of oxygen, or otherwise may apparently[5] first occur in the presence of metallic catalysts during attempted catalytic hydrogenation of the peroxides. Sorbic ester, α,δ-diphenylbutadiene, and probably elaeostearic ester, in the peroxides of which scission occurs respectively at the 3,4-, the 1,2 and the 9,10 or 13,14 double bond, are all examples of the spontaneous, unavoidable scission-type[6], and β,γ-dimethylbutadiene and isoprene of the catalyzed type[5]. Bodendorf reported that the last two dienes give (maximally) 0.47 and 0.32 mole, respectively, of formaldehyde or formic acid by the reductive treatment. The unavoidable scission at individual double bonds occurs side by side with the terminal peroxidation of the conjugated diene units, and its occurrence may be interpreted either as affording evidence that a corresponding degree of 1,2(3,4)-peroxidation accompanies the predominant 1,4-peroxidation, or as being due merely to some of the decomposing 1,4-peroxide molecules (thermally or catalytically activated) acting randomly as oxidizing agent for a proportion of the surrounding unperoxidized double bonds[7]. The high yield, however, of 1,2-scission which apparently occurred in Bodendorf's experiments during the catalytic hydrogenation of isoprene and dimethylbutadiene peroxides can only mean, if the stage at which the scission actually occurs is correctly interpreted, that breakdown of (presumably) the diradical $*O\cdot CH_2\cdot CMe{:}CH\cdot CH_2\cdot O*$ involves facile scission at the saturated $\underset{\alpha}{C}—\underset{\beta}{C}$ bonds.

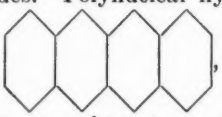
DISSOCIATING PEROXIDES

Dufraisse[8] and his coworkers have obtained much evidence to show that numerous polynuclear aromatic hydrocarbons containing the basic resonating system (F) yield photo-oxides (G), which can undergo thermal dissociation

above 120° into the original hydrocarbon and gaseous oxygen. Thus

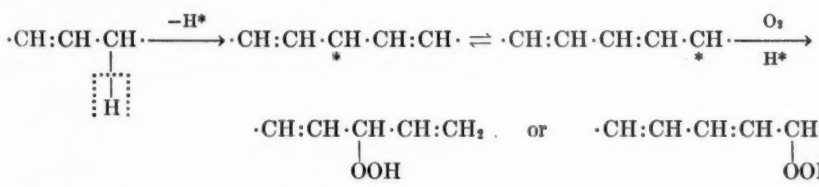


(F) (G)

when the C—O bonds in (G) are thermally severed, the oxygen succeeds in avoiding incorporation in (*i.e.*, avoids oxidation of) the unsaturated hydrocarbon system, and in this important respect the peroxides differ from all other known olefin peroxides. Polynuclear hydrocarbons, such as anthracene, and 6,7-benzanthracene,  , which do not exhibit aryl substitution at each of the meso-carbon atoms of an anthracene system, as occurs in (G), although they may, and often do, form peroxides in ultraviolet light, do not yield dissociating peroxides.

PEROXIDES OF LOW STABILITY

Di- and polyolefinic systems containing the 1,4-systems ·C:C·C·C:C·, ·C:C·C·C:C·C·C:C· etc., undergo during peroxidation extensive rearrangement of the double bond system to produce conjugated forms. Probably some degree of chain-scission accompanies the peroxidation, which at the beginning is of hydroperoxidic and mainly monomeric type, but later, as may be expected from the appearance of conjugated structures, passes to the production of viscous, doubtless polymeric forms. The monoperoxides are hydroperoxides in which the ·OOH groups are substituted at the ·CH_2· groups between the double bonds: thus the effective peroxidizing action, but not necessarily the initiating step, involves the detachment of α-methylenic H atoms. Such detachment enables the resonating radical residues to assume more stable, conjugated forms[9]:

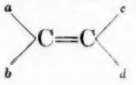


Monoölefinic systems autoxidize less easily, but appear to behave in a very similar manner, the products being hydroperoxides, in which the ·OOH groups are attached to α-methylenic carbon atoms. Here again resonance in

the radical 3-carbon systems appear ordinarily[10] to give pairs of isomeric peroxide forms:

$$\cdot CH_2 \cdot CH{:}CH \cdot \xrightarrow{-H^*} \cdot \overset{*}{C}H \cdot CH{:}CH \cdot \rightleftharpoons \cdot CH{:}CH \cdot \overset{*}{C}H \cdot \xrightarrow{O_2}$$

$$\cdot CH(OOH) \cdot CH{:}CH \cdot \quad \text{and} \quad \cdot CH{:}CH \cdot CH(OOH) \cdot$$

It is a significant fact that in monoölefinic systems the point of attachment of the ·OOH groups follows very faithfully the ordinary (polar) directives rules for ethylenic reactivity. Thus, just as in olefin addition-reactions, the course of reaction is largely or uniquely determined by the influence of the ethenic substituents on the polarization of the double bond, so the point of hydroperoxidation appears to be very precisely determined by the number and nature of the alkyl or aralkyl groups at the four ethenic positions *a*—*c*  so that (for example) in the systems:

$$RCH_2 \cdot CMe{:}CH_2, \quad RCH_2 \cdot CMe{:}CH \cdot CH_2R' \quad \text{and} \quad (RCH_2)_2C{:}CH \cdot CH_2R'$$

hydroperoxidation occurs most readily at the α-methylenic carbon atoms in heavy type[11]. Since the autoxidation process has with little doubt a radical, and not ionic, type of mechanism, the point of oxidative attack would seem to be determined wholly by the mesomeric condition of the olefin molecule.

$\Delta^{1,5}$-olefinic systems, $\cdot C{:}C \cdot C{:}C \cdot C{:}C \cdot$, $\cdot C{:}C \cdot C{:}C \cdot C{:}C \cdot C{:}C \cdot C{:}C \cdot$,

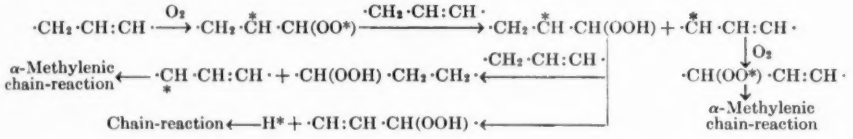
etc., such as occur in natural and synthetic rubbers, undergo hydroperoxidation at the α-methylenic positions, and both the ease and point of attack are greatly influenced by alkyl substitution at the ethenic positions, *e.g.*, the methyl groups in natural rubber facilitate hydroperoxidation at the C—atom in $\cdot CH_2 \cdot CMe{:}CH \cdot CH_2 \cdot$. Here, however, the presence of pairs of methylene groups between the double bonds precludes any very effective movement towards conjugation during peroxidation[12], since two successive double bond shifts, which would need to be promoted by two successive attacks by oxygen at the same pair of methylene groups, would be necessary to achieve it[9].

$$\cdot CMe{:}CH \cdot CH_2 \cdot CH_2 \cdot CMe \cdot CH \cdot \longrightarrow \cdot CMe{:}CH \cdot CH_2 \cdot CH{:}CMe \cdot CH(OOH) \cdot \longrightarrow$$
$$\cdot CMe{:}CH \cdot CH{:}CMe(OOH) \cdot CH(OOH) \cdot$$
$$\text{or } \cdot CMe(OOH) \cdot CH{:}CH \cdot CH{:}CMe \cdot CH(OOH) \cdot$$

THE PEROXIDATION MECHANISM

The hydroperoxidation of olefinic systems proceeds readily in nonionizing media, and it exhibits unmistakable signs of following a radical-actuated chain mechanism. Yet, although the reaction, whether photochemically or thermally promoted, is reported to be substantially pressure-independent and autocatalytic, it must be borne in mind that any detachment of an α-methylenic hydrogen atom from the olefin system to leave an active radical $\cdot \overset{*}{C}H \cdot CH{:}CH \cdot$ (the first likely stage in the production of an α-methylenic ·OOH group) requires the expenditure of about 80 kcal. of energy, which must be supplied from some not very obvious source; also it must be remembered that direct experiment shows that all investigated conjugated compounds, including those

in which the unsaturated centers are flanked by α-methylene groups, undergo peroxidation additively at the double bond systems, leaving the adjacent α-methylene groups intact. Since then it is clear (1) that molecular oxygen is intrinsically able to begin its attack at a double bond—presumably by adding to one end of it, (2) that the monomeric peroxides of simple olefins and of unconjugated polyolefins are in the main α-methylenic hydroperoxides, and (3) that the above-mentioned high expenditure of energy required at the outset of reaction for the dissociation of the C—H bond would be considerably diminished if oxygen were to begin its attack additively in some few of the olefin molecules and thereafter to continue the attack (substitutively) by means of chain reactions, there is perhaps good justification for postulating universal initiation of autoxidative attack in all the various kinds of olefinic systems by addition occurring at double bond centers, and for formulating the α-methylenic reaction characteristic of unconjugated olefins by the intermolecular scheme:



As thus envisaged the extent of actual addition at the double bonds of α-methylenic systems would be relatively insignificant, but would be sufficient to start the necessary reaction chains. It is to be noted that intramolecular reaction of a type permitting the first-formed diradical $\cdot CH_2 \cdot \underset{*}{CH} \cdot CH(OO^*)$ to become stabilized by detachment of hydrogen from the adjacent α-methylene group $[\rightarrow \cdot CH{:}CH \cdot CH(OOH) \cdot]$ is highly unlikely, since it would not propagate reaction chains. There is, however, some evidence accruing from observation of spontaneously occurring scission reactions which could be interpreted as indicating that two kinds of oxidative attack ordinarily occur in olefinic compounds side by side.

PEROXIDIC STRUCTURE AND TENDENCY TO CHAIN-SCISSION

Oxidative chain-scission sets in unpreventably with apparent ease at the very outset of the reaction of rubber with oxygen. This scission is responsible for the amazing fall in molecular weight from 350,000 to 80,000 during the absorption of <1 per cent of oxygen[13]. Other olefinic compounds display a similar tendency, and the question arises as to whether there exists a very direct mechanism of scission—one possibly running side by side with a quantitatively more important but less direct mechanism. A comparison of the overall consumption of oxygen by rubber with the number of scissions effected shows at once that the former is ample for a multistage and haphazard method of achieving the latter[13], but this does not exclude the possibility of a subsidiary direct mechanism.

Organic hydroperoxides, ROOH, are effective oxidizing agents for olefinic compounds, especially when their decomposition is thermally or catalytically facilitated. When, however, the oxidizing group and the susceptible olefinic structure occur in the same molecule the active oxygen contributed by the former is presumably most likely to be absorbed by the latter, although if that fails, intermolecular action is possible, and then the nature of the reactable

olefinic molecules present becomes of consequence to the overall reaction. It seems likely that the path pursued in the breakdown of peroxide groups is often independent of the way in which the released active oxygen is expended in olefinic attack (as would happen for instance if pairs of ·OOH groups were decomposed by mutual interaction, or if ·CH[OOH] groups split off water); otherwise the peroxide breakdown would be effected by direct interaction of peroxide groups with olefinic centers. Little study has, however, been given to the mechanism of decomposition of even saturated peroxides, and experience indicates that, in secondary autoxidation processes involving olefinic compounds, the overall course of reaction is much affected by experimental conditions, *e.g.*, the presence or absence of decomposition catalysts, acidity or alkalinity of medium, temperature and illumination. Thus olefin hydroperoxides decomposed in an acid medium have been found to pass extensively into triols, derived doubtless from the corresponding epoxides:

$$[\cdot CH(OOH)\cdot CH{:}CH\cdot \longrightarrow \cdot CH(OH)\cdot \underset{\diagdown\,O\,\diagup}{CH\cdot CH}\cdot \xrightarrow{H_2O} \cdot CH(OH)\cdot CH(OH)\cdot CH(OH){:}]$$

whereas those decomposed in an alkaline medium go a step further to give hydroxylated scission products (aldehydes, ketones and acids)[11]. Frequently ·OOH groups pass into ·OH groups and thereby contribute oxygen to the formation of epoxide groups; and this tendency extends to some thermally promoted interactions between olefin peroxides and olefins:

$$(R\cdot OOH + \cdot C{:}C\cdot \longrightarrow R\cdot OH + \cdot \underset{\diagdown\,O\,\diagup}{C\text{——}C}\cdot)$$

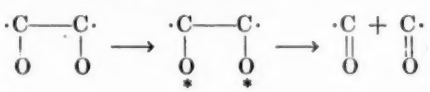
But epoxides are relatively stable saturated compounds, and there is little to show that their production necessarily or even usually precedes the final stage of autoxidative action, *i.e.*, chain-scission. At present, therefore, generalization with respect to the course pursued in thermal decomposition of olefin peroxides (or even of saturated peroxides in presence of olefins) is impossible.

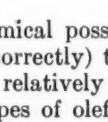
There remains the surprising fact that a considerable amount of facile and unpreventable scission ordinarily occurs at the α,δ-diphenylbutadiene, in addition to the more widespread attachment of oxygen at the ends of the conjugated diene system in each case. Since the 1,4-peroxidation of the conjugated diene is found to involve the addition of oxygen at the double bond system, the reaction presumably starts at one end of one double bond and may conceivably succeed in some degree and in some examples in linking up, at least momentarily, with the other end of the double bond attached:

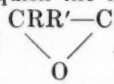
$$\cdot C{:}C\cdot C{:}C\cdot \xrightarrow[+\,O_2]{} \cdot C(OO^-)\cdot C{:}C \longrightarrow \underset{\text{minor product}}{\cdot C(O\cdot O)\cdot C{:}C\cdot} \quad \left[\text{or } \underset{\text{major product}}{\cdot C\cdot C{:}C\cdot C\cdot \ (\diagdown OO\diagup)}\right]$$

Such a 1,2-peroxide, if it were sufficiently stable to have more than momentary existence, might reasonably be expected to give the corresponding 1,2-diol on reduction, but in no single one of numerous examples studied has a reductively formed 1,2-diol been found. Any successful 1,2-linking oxygen which may

occur would seem to be of transient character and, so far as it occurs, probably undergoes ring-scission followed by scission of the carbon-chain:



A direct mechanism of this kind would be the most economical possible in oxygen and would explain simply (although not necessarily correctly) the apparent utter preventability of scission in examples where relatively stable peroxides form the main product. It could apply to all types of olefin and could function concurrently with the more normal peroxidation mechanisms formulated above. Paquot, in a recent study of the autoxidation of open-chain olefins[14] in presence of a peroxide-forming/peroxide-decomposing catalyst (nickel phthalocyanine), has obtained minor yields of the corresponding olefin epoxides with sufficient regularity to suggest to him that normal α-methylenic hydroperoxidation of monoölefins is in general accompanied by some (usually[15]) minor degree of 1,2-peroxidation to give coördinated forms: 

which readily relinquish the coördinated oxygen atom by secondary reaction, leaving the epoxide  . It is not at all clear, however, that the ring carbon atoms of Paquot's epoxides are normally those of the identical olefin peroxide molecules which supply the expoxido-oxygen, *i.e.*, that epoxide formation involves simple loss of oxygen from the parent peroxide.

THE POLYMERIC TENDENCY IN PEROXIDATION

The polymeric tendency referred to above with respect to conjugated olefins does not disappear entirely in the case of monoölefins and unconjugated di- and polyolefins, and in fact seems to be of rather general occurrence. Even in the most favorable examples of hydroperoxide formation there is usually an appreciable polymer fraction, and the yield of this appears to depend considerably on the nature and number of ethenic substituents. There are indications, however, that a part of this polymeric fraction consists of dialkyl peroxides of type: $R \cdot O \cdot R' \cdot$, doubtless formed in the manner: $R \cdot OO + RH \rightarrow R \cdot OO \cdot R' + H$.

THERMAL AND CATALYZED DECOMPOSITION OF PEROXIDES

Little detailed evidence is available, but it is very noticeable that various finely divided metals, metal derivatives and metal salts, *e.g.*, Pt, Pd, Fe or Ni phthalocyanines, Na_2SO_3 actively promote a type of peroxide decomposition which differs somewhat from the spontaneous decompositions (mainly thermal) ordinarily occurring in uncatalyzed autoxidations. This decomposition applies to monomeric and polymeric peroxides, and is especially characterized by the formation of $>CO$ groups in place of $>C(OH)$ groups.

The case of polymeric methyl elaeostearate peroxide has been mentioned above, and quite analogously, monomeric hydroperoxides of the cyclohexene

group will yield cyclohexenones. In the latter case the polymeric type of scission:

$$\cdot C\overset{\cdot\cdot}{H}R'\cdot O\overset{\cdot\cdot}{O}\cdot CHR\cdot \longrightarrow \cdot COR\cdot + RCH(OH)\cdot$$

is replaced by

$$\cdot C\overset{\cdot\cdot}{H}R(O\overset{\cdot\cdot}{O}H) \longrightarrow \cdot COR + H_2O,$$

so water is one scission fragment.

This paper forms part of a program of research undertaken by the Board of the British Rubber Producers' Research Association.

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[3] Thoms and Dobke, *Arch. Pharm. u. Ber deut. pharm. Ges.* **268**, 128 (1930); Bergmann and McLean, *Chem. Rev.* **28**, 367 (1941).
[4] The polymeric character, of course, precludes distillation at 10–15 mm. Their fractionation by molecular distillation has not been attempted.
[5] Bodendorf, *Ann.* **271**, 1 (1933).
[6] Farmer and Sundralingam, forthcoming paper; Sundralingam, in press.
[7] In this way, perhaps, the 1,2-epoxide, $HCPh\cdot CH\cdot Ch{:}CHPh$ (O bridging the CH and Ch), found in the autoxidation product from 8-diphenylbutadiene, and the 11, 12-epoxide, $H_5C_6\cdot CH{:}CH\cdot CH\cdot CH\cdot CH{:}CH(CH_2)_4\cdot CO\cdot(CH_2)_2\cdot CO_2R$ (O bridging the CH and CH), which seems to be a usual constituent of autoxidized licanic glyceride, are formed (see, however, below).
[8] Dufraisse, *Bull. soc. chim.* **6**, 422 (1939).
[9] Farmer, Sutton and Koch, *J. Chem. Soc.* **1943**, p. 541.
[10] Many indications of this are available, but formal verification has been obtained as yet only in the case of 1,2-dimethyl-Δ^1-cyclohexene (Farmer and Sutton, in press).
[11] This corresponds to the absence of any effective tendency toward conjugation on the part of $\Delta^{1,5}$-dienes under ionizing conditions, *e.g.*, when the dienes are heated with caustic alkali, although some degree of isomerization to $\Delta^{1,4}$-dienes may occur.
[13] Farmer and Sundralingam, *J. Chem. Soc.* **1943**, p. 125.
[14] Paquot, Thesis on "Autoxydation et Oxydation par l'Oxygène", Univ. of Paris, **1943**.
[15] In the case of conjugation arylethylenes, 1,2-peroxidation is held to be the major reactivity.

FRIEDEL-CRAFTS CATALYSTS AND POLYMERIZATION *

A. G. Evans, G. W. Meadows, and M. Polanyi

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In an earlier communication[1], evidence was given on which the following conclusion was based. In the dimerization of diisobutene and the polymerization of isobutene, it is essential that a trace of some third component, X, shall be present in addition to the monomer and the Friedel–Crafts catalyst, in order that the reaction shall proceed at an appreciable rate. It was suggested then that this third component was probably water. We have continued this line of investigation by studying the boron trifluoride-catalyzed polymerization of isobutene in the gas phase, using high-vacuum technique. The polymerization reaction was followed by mixing the boron trifluoride and the isobutene in the gas phase and measuring the fall in pressure with time. We may summarize the results as follows:

(1) The unpurified isobutene, taken straight from the cylinder, reacts rapidly when its pressure is greater than a certain value (Curve A).

(2) Isobutene, purified by many distillations from $-80°$ C to liquid air *in vacuo*, reacts very slowly under conditions which are otherwise identical with those for the experiments described in (1) (Curve B).

(3) The purified isobutene reacts rapidly if mixed with vapor of the residue from the distillation described in (2) (Curve C).

(4) This residue was identified as water by measurements of vapor pressure and freezing point.

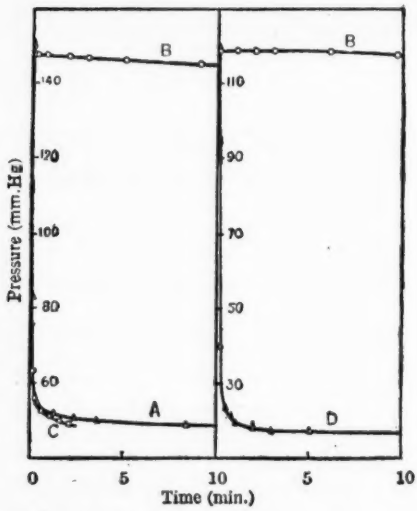
(5) Purified isobutene reacts rapidly if previously mixed with water vapor. As little as 10^{-1} mm. of water vapor is sufficient to give the rapid reaction (Curve D).

(6) When water is present with the isobutene in the gas phase, part of the boron trifluoride which is introduced into the mixture is removed by combination with the water. The boron trifluoride and water combine in practically equal molar quantities.

(7) When water had been added to purified isobutene to cause the rapid reaction in one experiment, the addition of boron trifluoride to the purified isobutene alone in the subsequent experiment was sometimes found to lead to rapid reaction. If the reaction vessel was pumped out for about half an hour between the two experiments, however, the purified isobutene used alone in the second experiment did not give the rapid reaction on addition of boron trifluoride.

We conclude from these experiments that for isobutene to be rapidly polymerized in the gas phase, the presence of both BF_3X and excess boron tri-

* Reprinted from *Nature*, Vol. 158, No. 4008, pages 94–95, July 20, 1946.



A, Unpurified isobutene; B, distilled isobutene; C, distilled isobutene plus 1 per cent residue vapor; D, distilled isobutene plus 0.1 per cent water vapor.

fluoride are necessary. In the experiments described in this communication, the third component, X, is water.

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[1] Evans, Holden, Plesch, Polanyi, Skinner and Weinberger, *Nature* **157**, 102 (1946).

MOLECULAR WEIGHT AND POLYDISPERSIVITY OF RUBBER BY DIFFUSION MEASUREMENTS *

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Laboratory of Colloid Chemistry, Karpov Institute of Physical Chemistry, Moscow, U. S. S. R.

The study of diffusion in solutions of natural rubber (light crepe) by Lamm's method[1] showed that even with a concentration of 0.1 per cent the normalized experimental diffusion curves diverge from the ideal Gaussian curve (Figure 1), in that they are characterized by a marked asymmetry and an excess of the maximal ordinate. It follows from an analysis of the experimental curves by the method of moments (up to moments of the fourth order) that they belong to Type IV Pearson curves, that is, to asymmetrical distribution curves with asymptotic branches. The determination of the perturbation multiplier enables us to calculate the course of the experimental curves with a fair degree of accuracy. The physical cause of asymmetry of the diffusion curves is the difference in the rate of diffusion to both sides of the interface (of the polymer into the solvent and back) due to a marked intermolecular interaction in the solution of the polymer at a given concentration. With a decrease of the concentration or of the molecular weight of the dissolved substance, the asymmetry of the diffusion curves becomes less pronounced. However, this asymmetry does not preclude the computation of the average diffusion coefficient D from the standard deviation of the curve. It can, indeed, be shown that the probable error does not exceed 1 per cent. The average value found for natural rubber in carbon tetrachloride is $D_{20^\circ} = 0.71 \times 10^{-7}$ sq. cm. per sec.

The asymmetry of the rubber molecules was calculated from the viscosity of rubber solutions by Simha's equation[2], the applicability of which for the computation of the ratio (b/a) of even highly asymmetrical particles with $b/a = 70$–90 has been verified experimentally with nitrocellulose[3]. The flexibility of the rubber molecules is here of no particular significance, as under the conditions of the experiment the forces of flow are below the critical value necessary for the deformation of the molecular coil[4]. Computation shows that for natural rubber $(b/a) = 117$–120 and $(f/f_0) = 4.35$–4.40. By combining the values of D and (f/f_0) by Polson's method[5], we find that, at a concentration of 0.116 per cent, the molecular weight of natural rubber is $M = 830{,}000$. Lansing and Kraemer's figure[6] obtained by the ultracentrifugation method for a 0.05 per cent solution is $M = 400{,}000$–$435{,}000$. In both cases aggregation in the solution undoubtedly occurs. Extrapolation of these results to $G = 0$ gives M equal to 130,000–150,000, which is presumably the true molecular weight of natural rubber.

Figures very close to this were obtained for natural rubber twice precipitated from a carbon tetrachloride solution by excess of alcohol, namely $D_{20^\circ} = 0.66 \times 10^{-7}$ sq. cm. per sec.; $b/a = 123$; $f/f_0 = 4.45$; $M = 970{,}000$ (at a concentration 0.135 per cent). After thermal destruction of rubber caused by

* Reprinted from *Nature*, Vol. 157, No. 3990, pages 518–519, April 20, 1946.

exposure for three hours to 140° in air the molecular characteristics changed abruptly: $D_{20°} = 1.6 \times 10^{-7}$ sq. cm. per sec.; $b/a = 88$; $f/f_0 = 3.85$; $M = 103{,}000$ (for a 0.135 per cent solution).

The following are the figures obtained for an industrial specimen of divinyl synthetic rubber: $D_{20°} = 2.1 \times 10^{-7}$ sq. cm. per sec.; $b/a = 65$; $f/f_0 = 3.31$; $M = 73{,}000$ (for a 0.112 per cent solution); the normalized diffusion curve has in this case a quite symmetrical character.

A comparison with the results of calculation of M from Staudinger's equation ($K_m^{\text{carb. tetrachl.}} = 3 \times 10^{-4}$) showed that at $M \sim 100{,}000$ and less this equation gives good agreement with M whereas with $M \sim 800{,}000$ the figures are several times less. Thus, for natural rubber $M_{St} = 193{,}000$ instead of 830,000, but for synthetic rubber $M_{St} = 68{,}000$ instead of 73,000. This result is in good agreement with data in the literature.

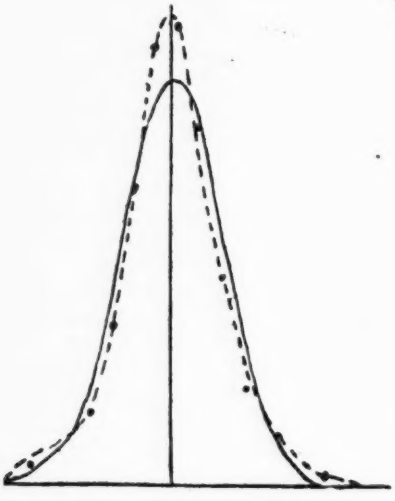

FIG. 1.—Gaussian curve (full line); experimental curve (broken line); calculated points (dots).

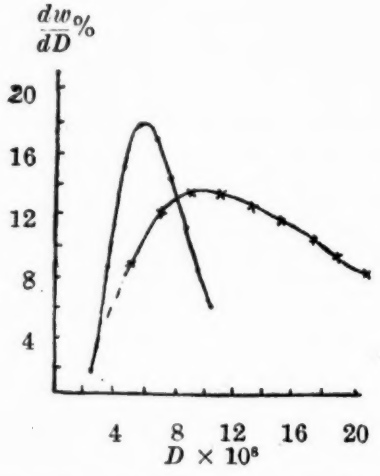

FIG. 2.—Curves for natural rubber (dots) and natural rubber after thermal destruction (crosses).

One can compute, on a model of an elongated ellipsoid, the length $l = 2b$ of the particles from the values of M and b/a. For natural rubber we obtain in this way $l = 3500$ A., whereas from the depolarization of diffused light l was found to be 3400 A. for the same system (0.1 per cent solution of natural rubber in carbon tetrachloride)[7].

Thus it appears that Polson's method can be applied to linear polymers over a wider range than might have been theoretically presumed.

All the rubber samples studied are characterized by an appreciable excess of the maximal ordinate of the normalized experimental diffusion curve over the ideal curve (this appears also from Figure 1), thereby indicating polydispersity of these substances. Gralén[8] suggested a convenient method of quantitative estimation of polydispersity as characterized by the ratio of the diffusion coefficients D_2/D_1 computed from the standard deviation and from the maxi-

mal ordinate of the diffusion curve. For a monodisperse substance, $D_2 = D_1$ or $D_2/D_1 = 1$; for natural rubber we have found $D_2/D_1 = 1.07$, after a twofold precipitation $D_2/D_1 = 1.18$, after thermal destruction $D_2/D_1 = 1.72$, etc. Assuming the logarithmic course of the distribution curve, one can, after Gralén, calculate from D_2/D_1 complete distribution curves (Figure 2), and thus obtain a more demonstrative picture of polydispersity of the substance. Finally, it can be shown that in the general equation for asymmetrical particles, $M = -K/D^a$, the value of a for natural rubber is 1.1 (for nitrocellulose Gralén obtained $a = 1.2$); whence it follows that for linear polymers the change of D follows very closely the change in the molecular weight.

On the whole, the application of the above methods to rubberlike polymers enables one to obtain from the diffusion and viscosity measurements a fairly complete molecular characterization of these substances. This is particularly significant for laboratories which do not possess an ultracentrifuge.

A full account of the work will be published in the near future in *Acta Physicochim. U.S.S.R.*

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PREPARATION AND PROPERTIES OF RUBBERLIKE HIGH POLYMERS. II. POLYMERIZATION OF MIXTURES IN BULK *

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INTRODUCTION

The polymerization of a homogeneous mixture, although more complicated than that of a single compound, involves easily reproducible reaction times, which is a considerable advantage when compared with the behavior of the same mixtures in emulsion. It is, therefore, frequently possible to produce a series of polymers of gradually changing composition from dienes and vinyl compounds which is suitable for study of the accompanying alterations in chemical and physical properties. Since such changes are affected not only by the initial ratio of diene to vinyl compound, but also by the experimental conditions, *e.g.*, temperature, catalyst, and yield, it is essential to evaluate kinetic conditions as a basis for comparison of the resulting polymers.

Three types of macromolecular compounds may be expected: (1) a true copolymer, (2) a purely mechanical mixture of separate polymers from the two components, and (3) a copolymer with a less regular pattern. As the rate of vinyl polymerization is higher than that of diene polymerization, catalytic conditions which favor the latter increase the chances of copolymerization. The first aim of our kinetic study was, therefore, to find a regular change in reaction rates with increasing vinyl content. Since all polymers proved to be either soluble or strongly swelling in suitable solvents, true copolymers could be easily distinguished from mechanical mixtures by their interaction with these liquids. The results of these two sets of experiments (kinetic measurements and solubility determination) will be given in the sections on polymerization and on interaction with liquids. The comparison of these copolymers with the products obtained by polymerization in emulsion will be made in Part V of this series.

The polymerization of dienes is hampered by the formation of cyclic dimers, and the same type of reaction between dienes and vinyl compounds is more pronounced in most cases; some new results with the Diels-Alder reaction will also be described.

POLYMERIZATION OF MIXTURES

In Part I[1] of this series we discussed the reaction rates of 2,3-dimethylbutadiene, isoprene, butadiene, styrene, and acrylonitrile, polymerized: (1) under the influence of natural impurities (heat polymerization), (2) with benzoyl peroxide (BP) as catalyst, and (3) with diazoaminobenzene (DAB) as catalyst. An investigation of all possible combinations would lead to at least 18 systems. The experiments which will be described refer only to combinations with buta-

* Reprinted from the *Journal of Polymer Science*, Vol. 1, No. 5, pages 353–363, October 1946. This is Communication No. 54 of the Rubber Foundation, Delft, Holland.

diene, the base for Buna rubbers, and dimethylbutadiene, which is particularly easy to handle and purify. Some runs were first made with a mixture typical for certain Buna rubbers (diene:vinyl compound = 7:3) in order to study the influence of catalytic conditions; further experiments with increasing concentrations of the vinyl compound were made only under optimum conditions.

Butadiene–Styrene.—Figure 1 gives a comparison of the rates for the mixture (7:3) and for the individual components. The reactivity of the mixture is comparable to that of pure butadiene. Yields, even in the presence of 1 per cent DAB, are considerably less than 100 per cent. From further preparatory

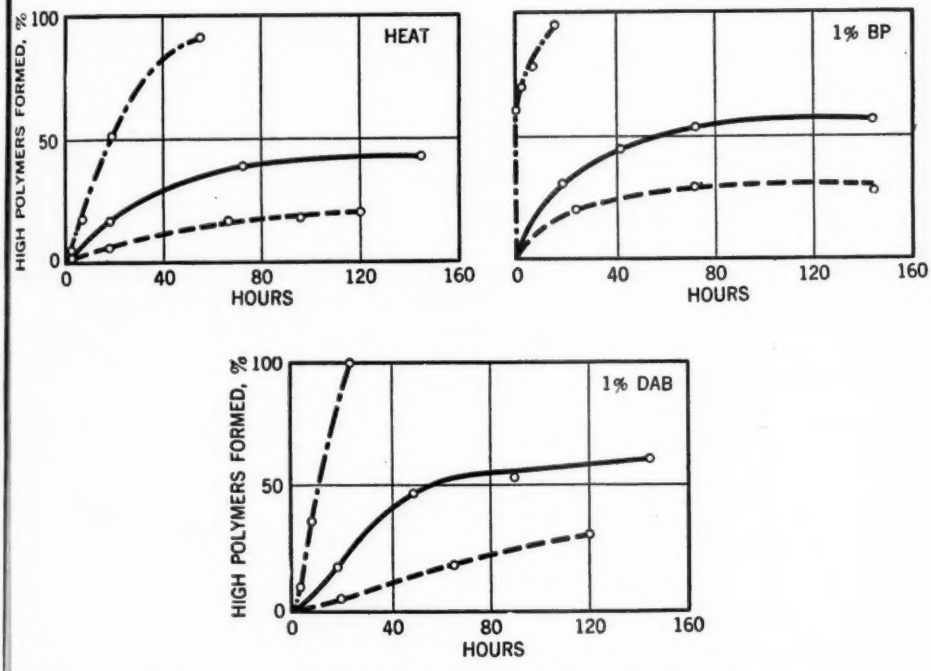

FIG. 1.—Polymerization of a mixture of 7 parts (by weight) of butadiene and 3 parts of styrene at 100° C: —, mixture; – –, butadiene; – · –, styrene.

experiments it is evident that the formation of cyclic dimers interferes with polymerization. Some of the butadiene, as well as some of the styrene, is used up by the dimerization reaction.

The resulting polymers differ from Buna-S only by having a much larger soluble fraction, but this property is also a function of the reaction time[1]. The mechanical properties of the vulcanized samples are in reasonable agreement with those of Buna-S.

Since the shape of the curves in Figure 2 indicates a very regular reaction course, the change of rate with increasing styrene concentration is expected to be gradual. The increase of yield with higher styrene concentration is caused by two factors: a higher reaction rate and a decrease in the dimerization reactions.

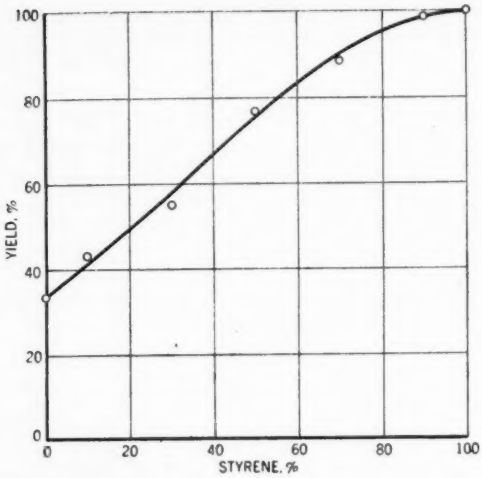

FIG. 2.—Polymer yields from mixtures of butadiene with increasing quantities of styrene after 150 hours at 100° C, with 1 per cent DAB as catalyst.

Dimethylbutadiene–Styrene.—Figure 3 shows that styrene accelerates the heat polymerization of dimethylbutadiene; as a consequence, the formation of dimers is somewhat superseded by the polymerization reaction. The rate with 1 per cent of DAB is sufficiently high to yield 100 per cent of polymer within a reasonable time, as in the case of the pure diene.

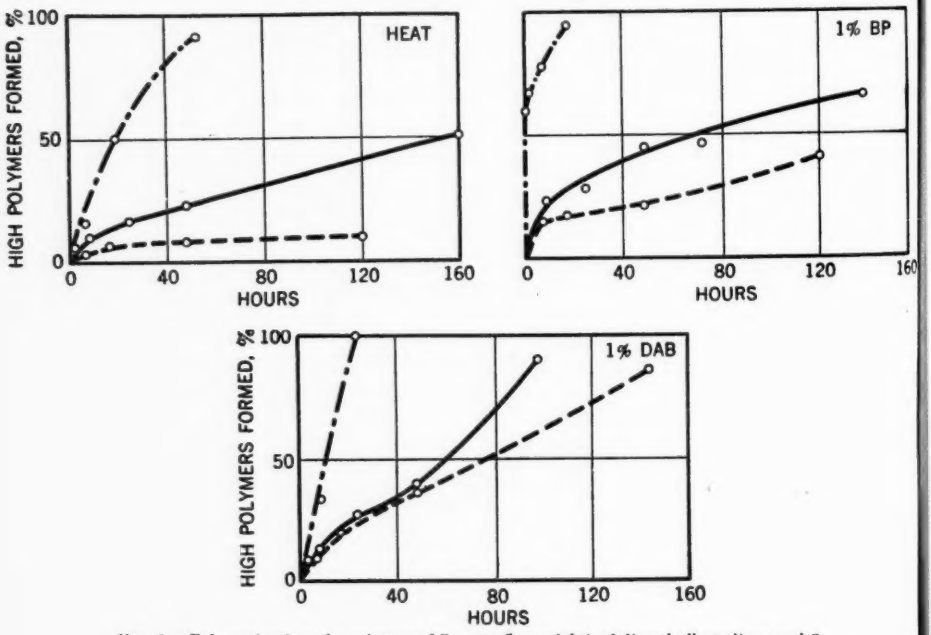

FIG. 3.—Polymerization of a mixture of 7 parts (by weight) of dimethylbutadiene and 3 parts of styrene at 100° C: —, mixture; – –, dimethylbutadiene; – · –, styrene.

The resulting polymers are all soft, soluble, and readily oxidized. Preliminary experiments with ethyl acetate as the solvent indicate that part of the yield consists of a mechanical mixture of polystyrene and methyl rubber. Further research was, therefore, temporarily discontinued.

Butadiene–Acrylonitrile.—Corresponding experiments with acrylonitrile lead to somewhat unexpected results. As may be seen from Figure 4, the yields of heat polymers are very low, due to a rapid Diels-Alder reaction between butadiene and acrylonitrile, which supersedes, not only the polymerization, but also the formation of cyclic dimers from pairs of butadiene molecules. The addition of catalysts has sufficient effect on polymerization to produce Perbunan as the main yield.

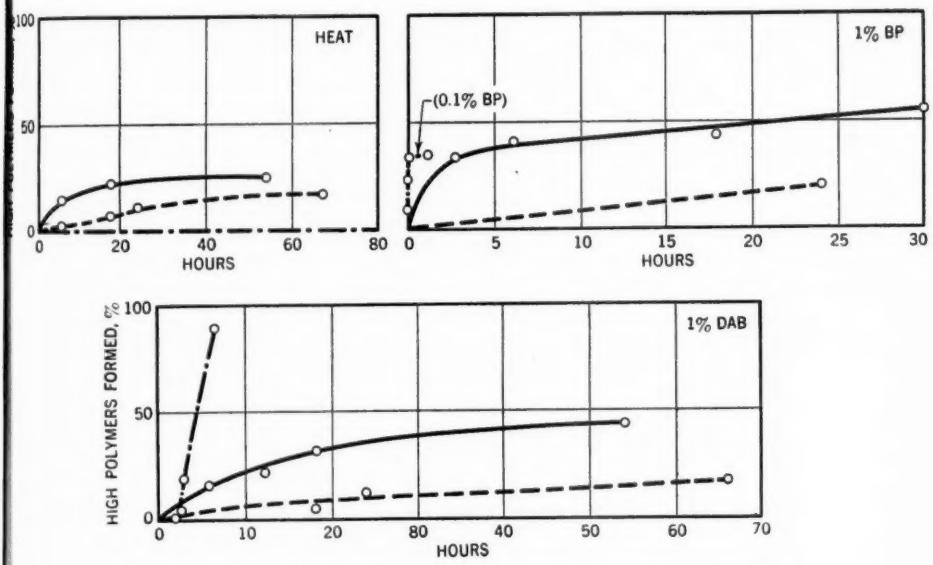

FIG. 4.—Polymerization of a mixture of 7 parts (by weight) of butadiene and 3 parts of acrylonitrile at 100° C: —, mixture; – –, butadiene; – · –, acrylonitrile.

This Perbunan differs from the commercial product only by having a greater solubility in certain organic liquids. The vulcanized samples have properties very similar to those prepared from the commercial product.

We have seen (Figure 4) that the addition of acrylonitrile has a highly accelerating effect on the polymerization of butadiene in the presence of catalysts. Nevertheless, in the range from 30 to about 80 per cent nitrile content, the mixtures catalyzed by 1 per cent of DAB react more slowly than is accounted for by the nitrile content. This discrepancy is the cause of the peculiar S-shaped curve of Figure 5, compared with the almost straight one of Figure 2. An explanation may, at least partly, be offered by the rapid Diels-Alder reaction between the diene and the nitrile, which competes strongly with the normal polymerization reaction. The nitrogen content of the polymers also indicates a loss of nitrile during the reaction (see Figure 6).

The properties of these polymers change gradually from those of a rubber-like substance at room temperature to those of a thermoplastic material which

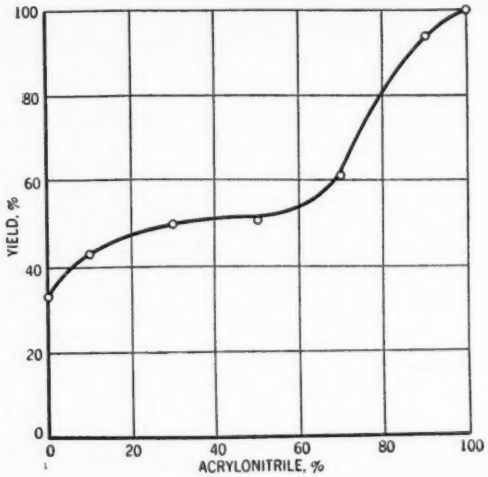

FIG. 5.—Polymer yields from mixtures of butadiene with increasing quantities of acrylonitrile after 150 hours at 100° C, with 1 per cent DAB as catalyst.

becomes elastic only at much higher temperatures. In the case of pure polyacrylonitrile, this temperature is higher than the limit of thermal stability.

Dimethylbutadiene–Acrylonitrile.—Analogous experiments with dimethylbutadiene lead to kinetically comparable results. The polymerization is

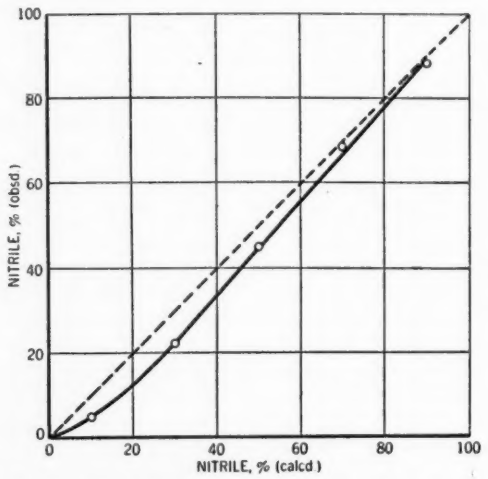

FIG. 6.—Difference between observed and calculated nitrile contents for copolymers from Figure 5.

strongly catalyzed by BP and by DAB, but is interfered with by dimerization. This is not the case with dimethylbutadiene alone, catalyzed by DAB, and our experiments show that the rate of dimerization between the diene and the nitrile is again higher than that between two molecules of the diene (see Figure 7).

The copolymers are soluble in strong solvents, *e.g.*, chloroform or toluene. Since polyacrylonitrile is insoluble and nonswelling in organic solvents, the possibility of formation of mechanical mixtures of methyl rubber and polymeric nitrile is excluded from these experiments. On the other hand, the polymers are completely precipitated by the addition of hexane to the solutions, which excludes the possibility of the presence of methyl rubber since the latter is soluble in this liquid.

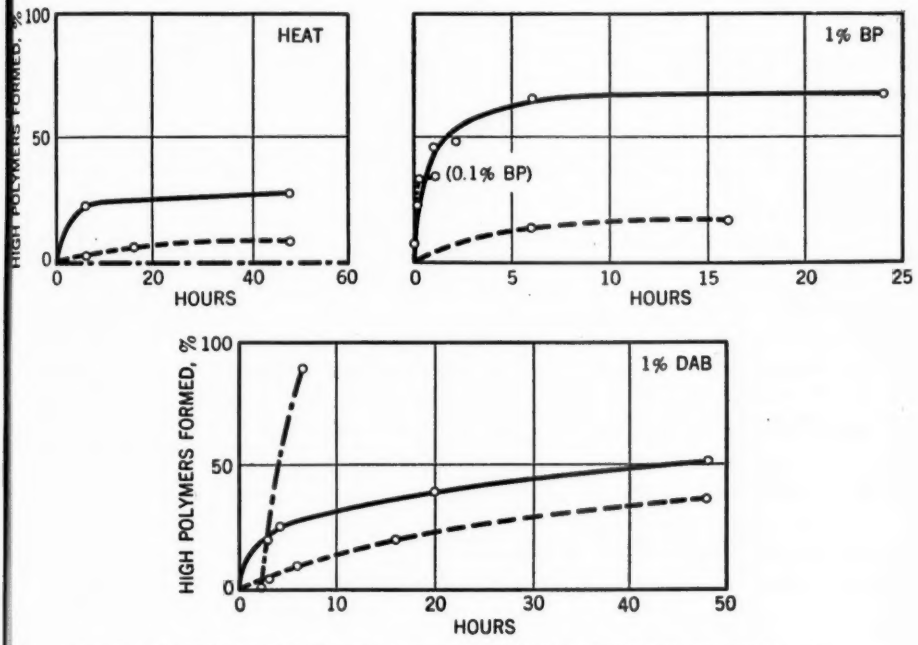

FIG. 7.—Polymerization of a mixture of 7 parts (by weight) of dimethylbutadiene and 3 parts of acrylonitrile at 100° C: —, mixture; – –, dimethylbutadiene; – · –, acrylonitrile.

The mechanical properties of these homologs of Perbunan are fundamentally different from those of Perbunan itself. At room temperature the polymers are hard and pliable, like gutta-percha, gradually showing increased elasticity at higher temperatures. These properties prove to be independent of the reaction time and of the method of preparation; more extensive experiments have, therefore, been made by polymerization in emulsion (Part III of this series).

DIELS–ALDER REACTION

The Diels-Alder reaction is an ordinary bimolecular one, the rate of which depends on the reactivity of both components, the dienes and the olefins. Since the three dienes used in these and the preceding experiments react both as olefins in the 1,2 or 3,4 position and as dienes, we can compare their reactivity with that of the vinyl compounds. Although typical differences may be observed, these reactions have a half-time of days or weeks at 100° C, which is very long compared to the time required for similar reactions with

maleic acid anhydride, which have a half-time of seconds or minutes at 20° C. Such major differences are doubtless due to much smaller heats of activation for the latter reactions.

The results of the work described here and in Part I of this series[1] are compiled in Table I; the structure of the dimers is given in Figure 8.

TABLE I

FORMATION OF DIMERS (DIELS-ALDER REACTION) AT 100° C AFTER 100 HOURS

Components				Yield		Structure of dimers (Figure 8) and composition of dimeric fraction
Diene	Vinyl compound	Ratio	Catalyst	Dimers (%)	Polymers (%)	
Butadiene	..	..	None	35	20	Exclusively *A*
			1% BP	30	30	
			1% DAB	25	40	
Isoprene	..	..	None	20	20	
			1% BP	..	40	Exclusively *B*
			1% DAB	..	40	
Dimethylbutadiene	..	..	None	10	20	
			1% BP	5	55	Exclusively *C*
			1% DAB	Traces	65	
Butadiene	Styrene	7:3	None	30	40	Mixture of about
			1% BP	20	55	60% of *A* and
			1% DAB	20	55	40% of *D*
Butadiene	Acrylonitrile	7:3	None	50	25	
			1% BP	25	60	Exclusively *E*
			1% DAB	40	40	
Dimethylbutadiene	Acrylonitrile	7:3	None	60	25	
			1% BP	25	60	Exclusively *F*
			1% DAB	30	50	

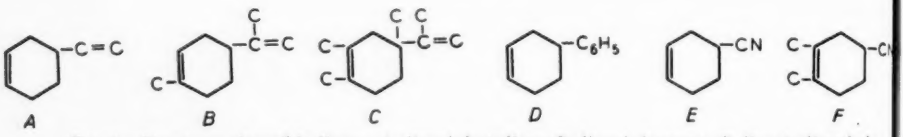

FIG. 8.—Structures of possible dimers: *A*, dimeric butadiene; *B*, dimeric isoprene; *C*, dimeric dimethylbutadiene; *D*, Diels-Alder product from one butadiene and one styrene molecule; *E*, Diels-Alder product from one butadiene and one acrylonitrile molecule; and *F*, Diels-Alder product from one dimethylbutadiene and one acrylonitrile molecule.

Taking the accuracy of our data into account, we can establish three separate series of increasing dienophilic reactivity.

(1) From Table V of Part I[1] we note that 35 per cent of dimers are formed during the heat polymerization of butadiene. About the same yield is obtained (30 per cent) when butadiene and styrene are copolymerized (in the ratio of 7:3) without a catalyst. Since, in this case, the dimeric fraction contains both possible compounds in the ratio of 6:4, we may say that the dienophilic reactivities of butadiene and styrene are the same magnitude. On the other hand, when butadiene and acrylonitrile (7:3) are copolymerized without a catalyst, a yield of 50 per cent of dimers is obtained; it appears, moreover, that the dimeric fraction consists almost exclusively of tetrahydrobenzonitrile. This means that the dienophilic reactivity of acrylonitrile is far greater than that of butadiene (about 10:1). We may accordingly give the following estimated rate relations with respect to the formation of cyclic dimers:

butadiene:styrene:acrylonitrile = 1:1:10

(2) The formation of cyclic dimers from dimethylbutadiene and acrylonitrile under the prevailing conditions of Table I is even more pronounced in the absence of catalysts than in the case of the lower homolog. We may, therefore, deduce the following ratio of dienophilic properties:

dimethylbutadiene:acrylonitrile = 1:10–15

(3) For the dimerization of the dienes themselves, the following ratios are derived from the values of Table I:

dimethylbutadiene:isoprene:butadiene = 1:2:3.5

Although no experiments were made with mixtures of the two dienes, the following complete series on the basis of increasing dienophilic properties is very probable from the data summarized above:

dimethylbutadiene	:	isoprene	:	butadiene	:	styrene	:	acrylonitrile
1	:	2	:	3.5	:	3.5	:	15–30

The slowest combination, *i.e.*, between two molecules of dimethylbutadiene, reacts with a half-time of weeks at 100° C, while the most reactive combination, between dimethylbutadiene and acrylonitrile, has a half-time of a few days at the same temperature. Differences between the two ends of the established series are, therefore, within a factor of 20. More accurate data are available from inhibition of polymerization, *e.g.*, by the addition of copper and manganese[2]. An attempt to offer a theoretical interpretation would be premature, since purely geometric factors may influence the rate, as well as changes in electronic arrangements.

It is evident that these side reactions make commercial production of such copolymers in homogeneous systems prohibitive. Polymerization in emulsion can be carried out at a much lower temperature, thereby greatly reducing the formation of cyclic dimers. This is one of the essential advantages of the emulsion method; the other important advantage is better heat dissipation in aqueous systems.

INTERACTION WITH LIQUIDS

The following experiments may serve as examples of the change in solubility and degree of swelling with increasing numbers of phenyl and nitrile groups in the polymers.

Butadiene–Styrene Copolymers.—Toluene is a strong solvent for both separate polymeric components; butanone is a strong solvent for polystyrene and a nonsolvent for polybutadiene; hexane is a weak solvent for polybutadiene and a nonsolvent for polystyrene.

Minimum solubility in toluene occurs when there is cross-linking of the polymers. Although the reaction times are the same, polymers with 30–70 per cent styrene are formed much faster and are, therefore, "older" at the moment of isolation than those from butadiene. Polybutadiene, isolated after 240 hours, is as insoluble as these copolymers[1]. With decreasing concentration of butadiene in the monomeric mixture, the statistical chances for side reactions (causing cross-linking) diminish and the copolymers remain soluble, although they are much "older" than the insoluble ones containing about 50 per cent butadiene.

Solubility is a function of both the molecular size and the number of polarizable phenyl groups in the molecule. In the case of hexane only the smaller

molecules of polybutadiene are soluble; the larger ones, which are soluble in toluene, remain in the gel fraction. The addition of only a few phenyl groups is sufficient to make all polymers insoluble in hexane.

Butanone is an associated liquid; in cases in which the ketone group can interact with a large number of polar or polarizable groups, it acts as a solvent.

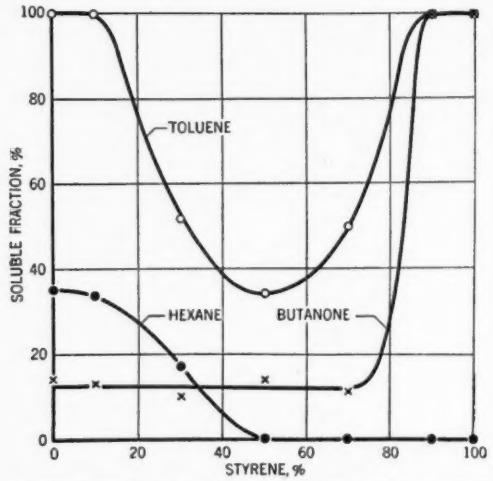

FIG. 9.—Solubility at 20° C for butadiene-styrene copolymers, prepared at 100° C with 1 per cent DAB, after 150 hours (see Figure 2).

As may be seen from Figure 9, a high concentration of phenyl groups, about one phenyl to three methylene groups, is necessary to dissolve all of the gel.

An even more significant picture is obtained from the swelling of the insoluble fraction. The weight fractions (the weight of swelling agent divided by the sum of the weight of swelling agent and the weight of polymers) are compared in Figure 10.

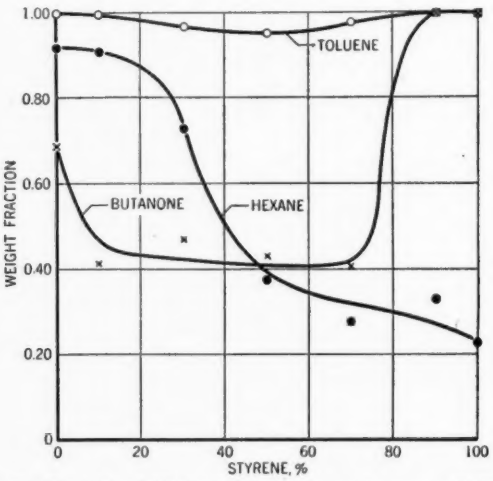

FIG. 10.—Swelling of insoluble fraction (solvents are the same as in Figure 9).

The interaction between toluene and the polymers now becomes essentially the same over the whole range of copolymers, while the fractions which are totally insoluble in hexane are still considerably swollen. The swelling in butanone is less significant, probably because the influence of molecular size and cross-linking somewhat counterbalances that of the polar groups. On the whole, a comparison of vulcanized samples (which will be given in a later communication) is more conclusive because the effect of molecular size is cancelled out by uniform cross linking.

Butadiene–Acrylonitrile Copolymers.—The situation is quite different for this system. The polymeric nitrile is not only insoluble but also nonswelling in all organic liquids at room temperature. In other words, a strong organic solvent for both components does not exist. The polymeric nitrile, however, is dissolved only by certain aqueous salt solutions, *e.g.*, lithium bromide, sodium thiocyanate, and zinc chloride[3], which fact proves the two-dimensional struc-

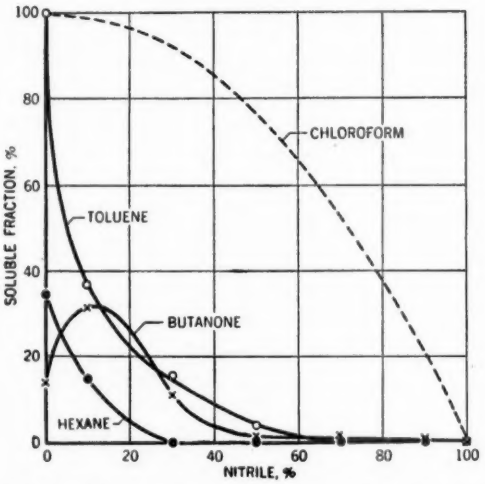

FIG. 11.—Solubility at 20° C for butadiene-acrylonitrile copolymers, prepared at 100° C with 1 per cent DAB, after 150 hours (see Figure 5).

ture of the macromolecules; those liquids, however, do not interact with the polymeric hydrocarbon. The most suitable solvent for the copolymers is chloroform, which dissolves, for the greater part, polymers containing up to 50–60 per cent of nitrile. Unfortunately, no quantitative experiments have yet been performed and we are, therefore, adding a schematic curve to complete the picture (see Figure 11).

We learn from Figure 11 that a few nitrile groups are sufficient to suppress solubility in these liquids. There are still great differences in the solvent action, as may be noted from the swelling equilibria given in Figure 12.

The interaction of the nitrile groups with the solvent decreases in the order: chloroform > butanone > toluene > hexane. The copolymers, which swell to an appreciable extent in the first three liquids, swell very slightly in hexane, a phenomenon typical for the oil-resistant properties of such rubberlike polymers.

These experiments show that differentiation between the effects of cross-linking and the specific action of polar groups cannot always be made from

solubility measurements alone, as may be seen from the properties of copolymers containing acrylonitrile. This case is, however, the only exception in the series of rubberlike copolymers and is due to the powerful associating forces of the nitrile groups. Because these groups are partly screened by the methyl groups

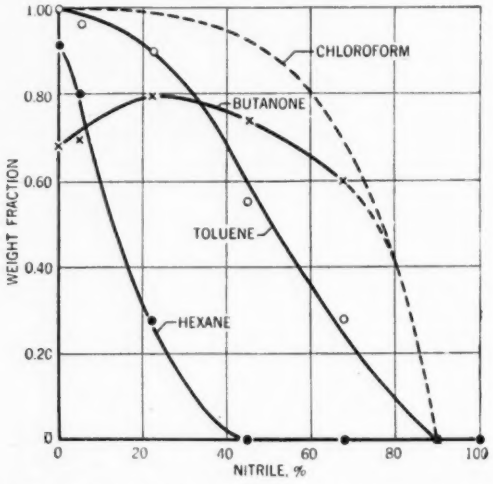

FIG. 12.—Swelling of insoluble fractions. The solvents are the same as in Figure 11.

in polymethyl acrylonitrile, the properties of this polymer must be comparable to those of polystyrene It may be expected, therefore, that the whole range of copolymers containing methyl acrylonitrile will remain soluble or swell strongly in chloroform and other weakly associated solvents. Detailed experiments with vulcanized samples will be described in further communications.

EXPERIMENTAL

The method of purification of the monomers and the polymerization procedure were the same as those described previously[4]. In some cases the polymers were precipitated with alcohol, while in others steam distillation proved to be more suitable for quantitative separation of the dimers.

The following examples may serve as an illustration.

Butadiene–Styrene.—After heating for 150 hours at 100° C, the gaseous monomer was allowed to escape. The polymers were subjected to steam distillation, and the resulting volatile compounds were fractionated after drying. The following fractions were separated.

Fraction	Temperature (° C)	Pressure (mm.)	n_D^{20}
I	133–136	760	1.4918
II	136–147	760	1.5040
III	40–50	15	1.5233
IV	115	15	1.5420

The high-boiling fraction IV is identical with 1,2,5,6-tetrahydrobiphenyl (Formula *D*, Figure 8), formed from one molecule of butadiene and one of styrene: carbon, 90.7% (calculated, 91.1%); hydrogen, 8.8% (calculated, 8.9%).

The lower boiling fractions contained monostyrene, some of which polymerized during redistillation. From fractions I–III a main fraction with the following properties was finally isolated: b.p.$_{760}$, 127.5–131.5° C; n_D^{20}, 1.4720. Monostyrene[5]: b.p.$_{760}$, 145.4° C; n_D^{20}, 1.5462; dimeric butadiene[6]: b.p.$_{760}$, 129.4° C; n_D^{20}, 1.4637.

This fraction therefore contains the cyclic dimeric butadiene (Formula *A*, Figure 8) which is formed simultaneously with the dimer from butadiene and styrene.

Butadiene–Acrylonitrile.—The dimeric fraction consists entirely of one compound, which proves to be 1,2,5,6-tetrahydrobenzonitrile. Elementary analysis: observed, C = 78.6%, H = 8.5%, N = 13.1%; calculated: C = 78.5%, H = 8.4%, N = 13.1%. B.p.$_{760}$, 192–196° C; n_D^{20}, 1.4732 (according to literature[2]); b.p.$_{760}$, 188–192° C; n_D^{20}: 1.472 (Formula *E*, Figure 8). Contrary to the results of the first experiment, no dimeric butadiene is present.

Dimethylbutadiene–Acrylonitrile.—The product was precipitated with alcohol, separated, and fractionated. Only one high-boiling compound was found: b.p.$_{760}$, 217–222° C; n_D^{20}, 1.4795.

The nitrogen content is in agreement with the assumed structure of 1,2,5,6-tetrahydro-3,4-dimethyl benzonitrile: N = 10.1% (calculated, 10.4%), see Formula *F*, Figure 8.

SUMMARY

Mixtures of butadiene and dimethylbutadiene with varying quantities of styrene and acrylonitrile were copolymerized under various catalytic conditions at 100° C. The formation of cyclic dimers from dienes and vinyl compounds is, in some cases, much more pronounced than the dimerization of the dienes alone. Since the latter is also a kind of Diels-Alder reaction, a series with increasing dienophilic properties can be established from a comparison of the yields of cyclic dimers. From solubility and swelling experiments it is evident that the polymers prepared from butadiene and the vinyl compounds and those from dimethylbutadiene and acrylonitrile are true copolymers. The mechanical properties of the copolymers from butadiene and increasing amounts of a vinyl compound change gradually from those of a rubber to those of the polyvinyl compound. The copolymers from a mixture containing 30 per cent styrene or acrylonitrile are very similar to Buna-S and Perbunan, respectively. Copolymers of the same composition from dimethylbutadiene and acrylonitrile, on the other hand, form a new class of thermoplastics with a much higher temperature of elasticity.

ACKNOWLEDGMENT

The authors wish to thank J. W. F. van't Wout for his assistance in carrying out the laboratory experiments.

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PREPARATION AND PROPERTIES OF RUBBERLIKE HIGH POLYMERS. III. POLYMERIZATION OF MIXTURES IN EMULSION *

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INTRODUCTION

Although synthetic rubbers are being produced by the hundreds of thousands of tons, very few papers are available on the preparation of such rubbers on a laboratory scale, except vague statements in the patent literature. The aim of the present paper is to fill this gap (at least partly) with reference to polymerization in emulsion. Previous communications dealt with polymerization in bulk[1]. Products made in the laboratory have several advantages over trade products for the study of physical and chemical properties. First, research becomes independent of the particular composition of a copolymer such as Buna-S. Second, a much better understanding of gradual changes may be obtained from study of a continuous series of copolymers which gradually change in properties from those of a polydiene to those of a polyvinyl compound. Third, the combination of dienes and various vinyl compounds may easily be altered, and much may be learned from the properties of certain products which are commercially uninteresting. Finally, by polymerizing the same mixture under a varity of experimental conditions, such as different temperatures, catalysts, emulsifying agents, and interruption after various reaction times, information may be obtained about the influence of these factors on the physicomechanical properties of the copolymers.

It is evident from the experiments described in the preceding papers that a very satisfactory reproducibility of reaction times can be reached as long as the impurities of the reagents are kept constant. Working with emulsions, the situation becomes more complicated. As will be explained below, the actual concentration of the catalyst is not strictly reproducible and the reaction time, therefore, becomes more dependent on small changes in experimental conditions.

We shall first explain the essential meaning of reproducible reaction times with respect to the physicomechanical properties, following a line of thought developed by Dogadkin and his coworkers.

The quality of a rubber can only be given in arbitrary units; we shall take the quality of natural rubber as 100. Polybutadiene is on the whole a very poor rubber, because of several serious shortcomings. Nevertheless, its quality changes considerably with reaction time from that of a sticky and therefore mechanically weak product at low yields to a material of moderate quality at yields of, *e.g.*, 50–80 per cent. Finally, after still longer reaction times, products are isolated which again exhibit poor qualities—as a consequence of strong cross-linking. These final products, however, are hard and brittle

* Reprinted from the *Journal of Polymer Science*, Vol. 1, No. 5, pages 364–379, October 1946. This is Communication No. 53 of the Rubber Foundation, Delft, Holland.

and, therefore, mechanically useless. Such changes have been found in products prepared in homogeneous systems, as well as in others prepared in emulsions. Although all these rubbers are of inferior quality, a distinct optimum, which corresponds to a yield of about 80 per cent may be distinguished. The situation is illustrated schematically in Figures 1 and 2.

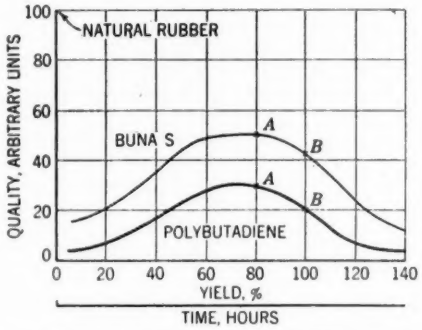

FIG. 1.—Changes in rubber quality (arbitrary scale) with increasing yields and reaction times during the preparation of polybutadiene and Buna-S. *A*, point at which optimum quality is obtained; *B*, 100 per cent yield.

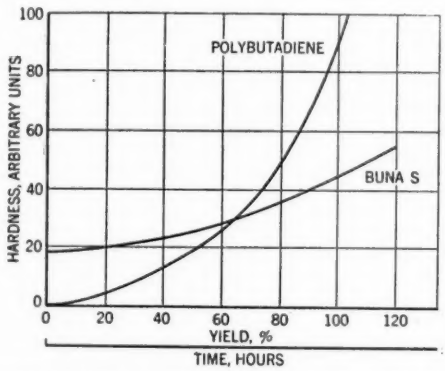

FIG. 2.—Changes in hardness of synthetic polymers (arbitrary scale) with increasing yields and reaction times, corresponding to Figure 1.

During the preparation of Buna-S, the same type of changes are encountered, but the rate of cross-linking which occurs during polymerization is reduced in comparison with that of butadiene. The position of the optimum in qualities is, therefore, higher, but still far below that of a pure gum mixture of natural rubber. A schematic comparison for this case is also given in Figures 1 and 2.

The difficulties in reproducing a rubber of optimum quality (*A* in Figures 1 and 3) by polymerization in emulsion may be readily understood from Figure 3. Three types of time–yield curves are possible: (1) a smooth curve, *1*, in which case very similar yields can be reproduced at constant reaction times; (2) a reaction with a long induction period and an explosive polymerization, represented by curve *3* (it is very difficult to obtain similar yields at constant reaction times, because of the variability of the induction period); (3) an intermediate case, illustrated by curve *2*.

Since the rate of the reaction depends on the actual concentration of catalysts, the situation becomes still more complex because of variations in experimental conditions, such as stirring or shaking the emulsions.

To overcome these difficulties, we preferred to work with reaction times very near 100 per cent yield (*B* in Figure 3). At such a point reproducibility apparently becomes much better, since practically no difference in yields is found between points *B* and B_1. Such variations are not essential for comparisons of certain properties, *e.g.*, the swelling of vulcanized samples, because in this case these variations are flattened out by the curing process. In comparing the mechanical properties of our polymers with those of commercial products, the significance of points *A* and *B* in Figures 1 and 2 should be kept in mind.

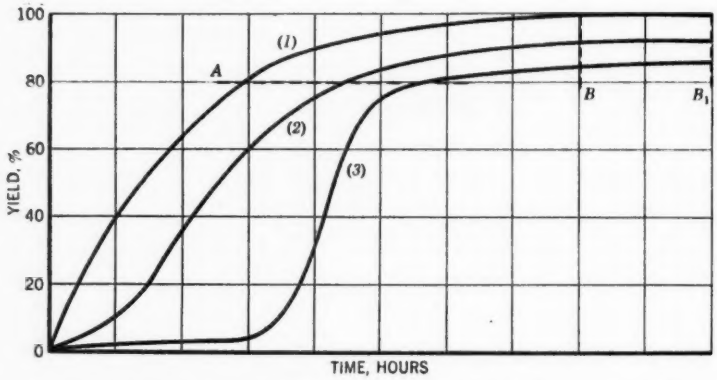

FIG. 3.—Possible shape of yield–time curves for the preparation of the rubbers described in Figures 1 and 2. *A*, point at which optimum quality is obtained; *B*, 100 per cent yield.

Batches of commercial Buna-S also vary considerably in the mechanical properties of both the raw and the vulcanized rubber. The causes of such variations, which are considerably larger than those found in standardized natural rubber, are likely to be of the same nature as those just discussed.

As the reaction time for polymerization in emulsion sometimes depends on such factors as the number of turns of the shaking machine employed, the absolute value of the percentage yield at a definite time is only significant as long as the experiments are performed under exactly the same conditions. We shall, therefore, first illustrate the essential points in evaluating reaction rates by a number of examples in the section on the kinetics polymerization. Some of the properties of the polymers thus obtained will then be discussed in another section, while those of the vulcanized samples will be given in the fourth and fifth papers of this series.

KINETICS OF POLYMERIZATION

GENERAL REMARKS

In the case of dienes the term polymerization is frequently employed with very different meanings: (1) as a chain reaction started by catalytic action and leading from many small, monomeric molecules to relatively few, large, more or less threadlike, polymeric molecules; (2) as a very short chain of reactions taking place between only a few reactive vinyl groups present in the side chains of

the previously formed macromolecules (as a consequence of simultaneous 1,4 and 1,2 addition)—this chain is also initiated by catalytic action; (3) as an ordinary bimolecular substitution-addition at a methyl or methylene group of the macromolecules in α-position with respect to the double bond and, therefore, containing very reactive allyl hydrogen atoms (this latter reaction may occur not only under the influence of catalysts, but also with a great variety of reagents).

Since it is possible to interlink threadlike macromolecules by the reaction mechanisms of (2) and eventually (3), as well as to modify the general structure of the macromolecules, such secondary reactions contribute greatly to the gradual changes in properties of polydienes during polymerization and result in the optimum in qualities, which has been pointed out above. Synthetic rubbers in general, and copolymers of butadiene in particular, clearly show such secondary polymerization reactions. The latter possess many unsubstituted vinyl groups, while the polymers of isoprene and dimethylbutadiene, respectively, contain methyl-substituted vinyl groups. In the latter configuration, allyl hydrogen atoms are also present in the side chains. This structural difference offers a possible explanation for the stronger tendency of polybutadiene to undergo cross-linking, for in this case the catalyst acts exclusively as a promoter of the polymerization, *i.e.*, cross-linking reaction (mechanism 2), while in the second case it may also react with the active hydrogen atoms of the methyl groups (mechanism 3) without causing cross-linking.

On the whole, this readiness to undergo further polymerization is a technical disadvantage of the synthetic products. Natural rubber has no reactive vinyl groups in side chains; it possesses only double bonds in the main carbon chain, which are less sensitive toward free radicals than its extremely reactive α-methylene groups[2]. As a consequence degradation phenomena are predominant with this material, while it is more difficult to produce them with polymers from butadiene.

MECHANISM OF CATALYSIS

The general scheme for a polymerization—a sequence of three reactions, starting, chain, and terminal reactions—is also valid for emulsions. The difficulty in understanding the details arises from the uncertainty about the nature and the actual concentration of the catalyst. None of the comparatively simple relations which are valid for the interaction of catalysts and monomers in homogeneous systems are applicable to emulsions. The catalyst added to the emulsion may act as a source of free radicals but the interaction in the emulsion among the monomer, catalyst, oxidation products, emulsifying agent, and water, is of such a nature that a change in the concentration of any component proves to be a rate-determining step.

The most obvious difference between reactions in emulsions and in homogeneous systems is the acceleration of the polymerization. The catalyzed polymerization of dienes in bulk takes several days at 100° C. Even in suspension (without an emulsifying agent), the polymerization of styrene with BP takes several hours at 90° C[3]. When dienes are emulsified, polymerization is complete in a few days at 50° C; while, after mixing with vinyl compounds, one can reach a nearly quantitative yield in the same time at room temperature. As will be seen from the following, this is partly due to an apparently smaller heat of activation, but this factor alone would not be sufficient to account for the extraordinary acceleration of the reaction; there must also be a

much higher statistical factor (which is independent of temperature) favoring the reaction. The situation is illustrated by Tables I and II.

TABLE I

INFLUENCE OF EMULSIFYING AGENTS AND CATALYSTS ON RATE OF POLYMERIZATION OF A SINGLE MONOMER *

Expt. No.	Temp. (° C)	Time (hours)	Emulsifying agent	Catalyst (percentage calculated on monomer)	Yield (%)
1			None		0
2			Igepon T		17
3	50	80	Sapamin CH	None	26
4			Sulfonated hydrocarbon		67
5			5% ammonium linoleate		50
6			5% Fixanol		80
7				None	14
8				1% DAB	50
9	50	17	5% ammonium linoleate	1% hydrogen peroxide	53
10				1% persulfate ion	56
11				1% BP	24
12				None	4
13	36	46	5% ammonium linoleate	0.01% hemin	13
14				0.5% hydrogen peroxide	42
15				0.5% persulfate ion	48

* Shaking machine, 80 turns per minute; Jena glass tubes, 10–50 cc. content; 3 parts (by volume) of butadiene and 7 parts (by volume) of aqueous solution.

Taking butadiene as a standard monomer, we learn from Experiments 1–6 of Table I that a variety of emulsifying agents cause polymerization without a catalyst. Neither the stability of the emulsion nor the *p*H of the medium has a definite influence on the rate. The accelerating effect of the emulsifying agent can be increased by a variety of catalysts, among which DAB, hydrogen peroxide, and persulfate ion are about equally effective (Experiments 7–11).

The temperature dependence is about 2 for 10° C (experiments 12–14). The addition of traces of iron in the form of a complex compound has a distinctly favorable effect under these conditions (even more at lower temperatures), but it is not always very pronounced.

Further experiments, which are not reported here in detail, lead to the conclusion that the reaction rate of dimethylbutadiene is very similar to that of butadiene, but various factors do not always have the same effect on the two types of emulsions.

Styrene is only about three times more reactive than butadiene at 50° C, even with peroxide as a catalyst. This is a very small difference in reactivity between these two compounds as compared with the remarkable effect of BP on styrene in homogeneous systems. The polymerization of styrene affords only a very small heat of activation in emulsion, corresponding to a factor of 1.5 for 10° C. Consequently, high yields of polystyrene can be produced after a few hours at 36° C.

While the polymerization of these monomers proceeds quite smoothly, acrylonitrile behaves anomalously. As was stated in Part I[1] of this series, the pure nitrile is perfectly stable, but a vigorous polymerization occurs under the influence of traces of catalysts. Even after prolonged heating at 100° C in the presence of catalysts, the emulsified nitrile sometimes resists polymerization or is used up in side reactions; in pure water, on the other hand, polymerization

TABLE II

COPOLYMERIZATION IN EMULSION *

Expt. No.	Mixture	Temp. (° C)	Time (hours)	Emulsifying agent	Catalyst (percentage calculated on monomeric mixture)	Yield (%)
16	7 parts butadiene and 3 parts styrene (by wt.)	50	18	5% ammonium linoleate	1% DAB	30
17		50	18	5% ammonium linoleate	1% persulfate ion	37
18		50	18	10% ammonium linoleate	0.01% hemin	50
19		50	18	10% ammonium linoleate	1% persulfate ion	68
20		50	18	10% ammonium linoleate	0.01% hemin 1% persulfate ion	78
21		36	46	5% ammonium linoleate	None	12
22		36	46	5% ammonium linoleate	0.5% persulfate ion	54
23		36	46	10% ammonium linoleate	0.5% persulfate ion	66
24		18	216	10% ammonium linoleate	1% persulfate ion	44
25		18	216	10% ammonium linoleate	1% DAB	15
26		18	216	10% ammonium linoleate	1% DAB 0.01% hemin	24
27	7 parts butadiene and 3 parts acrylonitrile (by wt.)	50	18	5% ammonium linoleate	0.5% persulfate ion	41
28		50	18	5% sodium oleate	0.5% persulfate ion	87
29		50	18	5% Fixanol	0.5% persulfate ion	90
30		36	18	5% sodium oleate	1% persulfate ion	89
31		23	110	5% sodium oleate	1% persulfate ion	91
32	7 parts dimethylbutadiene and 3 parts acrylonitrile (by wt.)	50	18	5% sodium oleate	0.5% persulfate ion	100

* All experimental mixtures contain 3 parts (by volume) of monomeric mixture and 7 parts (by volume) of aqueous solution; other experimental conditions correspond to those of Table I.

takes place at 50° C. According to a patent specification[4], acetylene acts as a regulating agent and we have found that the addition of dienes to the nitrile also has a favorable effect on a smooth and reproducible course of reaction. Addition of small quantities of nitrile to the diene also leads, on the other hand, to an increase in rate. Such systems are described in Table II; we find that the fastest ones contain dienes.

From a comparison of experiments 16–20 and 21–23 with, respectively, 7–11 and 12–15 (Table I), we note that the addition of styrene to butadiene has no appreciable accelerating influence (and sometimes even a retarding effect) on the reaction rate. The temperature dependence seems to be somewhat smaller than that of the diene alone and the reaction can be observed conveniently at room temperature (Experiments 24–26).

The addition of acrylonitrile causes a distinct increase in rate, which is particularly pronounced at lower temperatures (Experiments 27–31). The last experiment in Table II demonstrates the still higher reactivity of a combination of the nitrile with dimethylbutadiene.

We shall now try to explain the high absolute value of reactions in emulsions, at least on a qualitative basis. The influence of temperature on the polymerization of dienes and styrene indicates a somewhat smaller heat of activation in the case of emulsions than in that of homogeneous systems; since, however, the rate is many thousand times faster, a more favorable statistical factor, which is independent of the temperature, of at least 10^3 also must contribute to the increased rate.

As the overall rate may depend on the ratio of the rate of (aut)oxidation to the rate of the starting reaction, an increased rate of autoxidation of the hydrocarbons in emulsion, *e.g.*, as a consequence of shaking, contributes correspondingly to the number of starting reactions. There is little doubt that, in all cases in which the monomer can be oxidized, the mechanisms of the starting reaction and the chain reaction do not differ much from those in homogeneous systems. But the very small temperature dependence of the copolymerization with acrylonitrile, as well as the particularly sluggish response of the nitrile itself, indicates the occurrence of a different phenomenon in these latter cases. Quite recently this situation has been clarified by essential contributions from British authors.

Bacon proved the polymerization of acrylonitrile to be sensitive to redox systems and the polymerization of the nitrile in a homogeneous aqueous solution has a perfectly regular character in the presence of certain reducing agents, *e.g.*, thiosulfate, and with the exclusion of air[5]. Morgan demonstrated that side reactions of the nitrile can interfere with polymerization[6], which agrees well with our own observation that the polymeric nitrile sometimes contains considerable quantities of oxygen. Evans and coworkers finally proved that the rate-determining step is an electronic transfer reaction of the type discovered by Haber and Weiss[7]:

$$H_2O_2 + Fe^{++} \longrightarrow HO + HO^- + Fe^{+++}$$
$$HO + Fe^{++} \longrightarrow HO^- + Fe^{+++}$$
$$HO + H_2O_2 \longrightarrow H_2O + HO_2$$

in which the monomer acts as a consumer of the OH and HO_2 radicals[8]:

$$HO + CH_2{=}CH \longrightarrow HO{-}CH_2{-}\underset{\displaystyle X}{\underset{|}{CH}}{-}$$

$$HO{-}CH_2{-}\underset{\displaystyle X}{\underset{|}{CH}} + CH_2{=}CH \longrightarrow HO{-}CH_2{-}\underset{\displaystyle X}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle X}{\underset{|}{CH}}{-}$$

Such a reaction is sensitive to reducing agents, since the latter influence the actual concentration of the radical; the poisoning effect of oxygen can be understood as a reaction between ferrous ions and oxygen. The activation energy for the transfer of an electron is only about 8–10 kcal., which fact partly explains the accelerated rate in aqueous solutions of the nitrile; the high absolute value of reactions in emulsions still needs further and more quantitative explanations[9].

EMULSIFYING AGENTS AND CATALYSTS

Since Buna-S contains considerable quantities of linoleic acid, we started with a comparison of the soaps of stearic, oleic, and linoleic acids. It was clear from the work of Dogadkin and his associates that alkali salts are preferable to other metal soaps, and that the experiments must be conducted in glass tubes because traces of heavy metal ions from a steel autoclave may interfere with the catalysts[10]. Actually, it proved difficult to reproduce an experiment in an autoclave, and all experiments were, therefore, conducted in glass containers. Our experiences can be summarized as follows.

(1) Stearic acid soaps are much more viscous than oleate or linoleate soaps of equal concentration and stable emulsions are produced. Stearic acid is frequently squeezed out of the rubber and, since these soaps offer no kinetic advantage over the others, further experiments were limited to soaps from the unsaturated acids.

(2) The rate in oleic and linoleic soap emulsions also depends on the metal ion, but no distinct difference among sodium, potassium, and ammonium ions can be detected, because the influence of concentration and temperature, as well as the structure of the monomer, also affect the rate; *e.g.*, with dimethylbutadiene, oleic acid soaps were most effective, while, with butadiene, linoleic acid soaps had a greater catalytic action. Trimethylammonium soaps retarded the reactions, which is in contradiction to observations for other vinyl compounds.

(3) The reaction rate is very sensitive toward a change in the concentration of the soaps. Solutions of 5 per cent (by weight of the soap) are most suitable at 50° C; a concentration of 10 per cent results in emulsions of greater stability, but the rubbers contain more of the emulsifying agent. At room temperature, 10 per cent soap solutions are preferable, since occasional shaking is sufficient to keep the hydrocarbon emulsified. The ratio of the volume of monomer to the volume of soap solution is also a rate-determining factor, with an optimum between 3:7 and 4:6.

(4) Coagulation with methyl alcohol, or a combination of methyl alcohol and sodium chloride, and consecutive washing of the polymers leads only to partial removal of the soap. Generally, the particles of the latex are much smaller than those of natural rubber, which accounts for the fact that these polymers, as well as commercial Buna-S, contain about 5 per cent or more soap.

(5) Fixanol, which is essentially cetylpyridinium bromide, is an effective emulsifying agent as well as a catalyst, but no obvious advantage has been observed from the use of an acid medium; on the contrary, the polymers are frequently more highly cross-linked than those prepared in an alkaline medium.

(6) Many other emulsifying agents, *e.g.*, commercial products such as the Sapamins (Ciba) or sulfonated hydrocarbons, may be used, but most of them are less suitable than soaps. In agreement with claims made in the patent literature, we have found that combinations of two emulsifying agents are frequently more effective than the single components.

From these results we may conclude that the sodium soaps of oleic and linoleic acids are the most convenient agents for our purposes.

As no attempt was made to exclude the presence of peroxides, or the formation of peroxides during polymerization, it seems reasonable to assume that all emulsions contained a small but very effective amount of labile peroxides. Experiments on the rigid exclusion of oxygen should supply more information on the real influence of phase boundaries on the reaction rate. The influence

of intentionally added catalysts was considerable, as may be seen from Tables I and II and the drawings given in the next section. The following conclusions may be drawn from our data:

(7) Hydrogen peroxide and persulfates added in concentrations of 0.5–1 per cent (calculated on the amount of monomer present) are very effective accelerators. Between 50–100° the reaction rate of the uncatalyzed reaction is from ten to several hundred times smaller than that of the intentionally catalyzed reaction. Such differences are even more pronounced at room temperature.

(8) Dogadkin has shown that DAB is a powerful catalyst for the polymerization of butadiene[11]. We can confirm these results, but, working with monomers of a considerably higher purity than the butadiene of Dogadkin, we found that peroxides were frequently as effective as DAB. The activity of the latter catalyst at lower temperatures is difficult to understand and a simultaneous interaction with peroxides may be assumed.

(9) As may be seen from Tables I and II, traces of substances containing iron in a complex form, *e.g.*, hemoglobin, sometimes act as specific accelerators, which is in agreement with claims made in the patent literature[12].

(10) As the polymers tend to become more cross-linked with increasing concentrations of the catalyst, 0.5–1 per cent is likely to be the optimal concentration.

Summing up, we may conclude that the addition of 0.5–1 per cent of peroxides or DAB is a suitable method to shorten the necessary reaction time.

PREPARATION OF COPOLYMERS

Butadiene–Styrene.—We stated previously that polymerization of mixtures of dimethylbutadiene and styrene results in polymers consisting chiefly of mechanical mixtures of the polydiene and polyvinyl compound; our investigations were, therefore, limited to the copolymers of butadiene and styrene.

The polymerization of mixtures from these monomers proceeds very smoothly, as may be seen from Figures 4–6. The yield–time curve in Figure 4 corresponds to type (1) of Figure 3. Since the butadiene used contained gaseous impurities[1], ultimate yields may be expected to fall well below 100 per cent. On the other hand, part of the emulsifying agent becomes incorporated in the polymers, which sometimes causes apparent yields above 100 per cent.

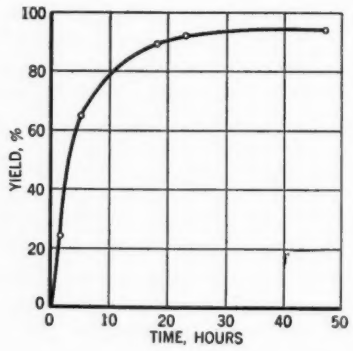

FIG. 4.

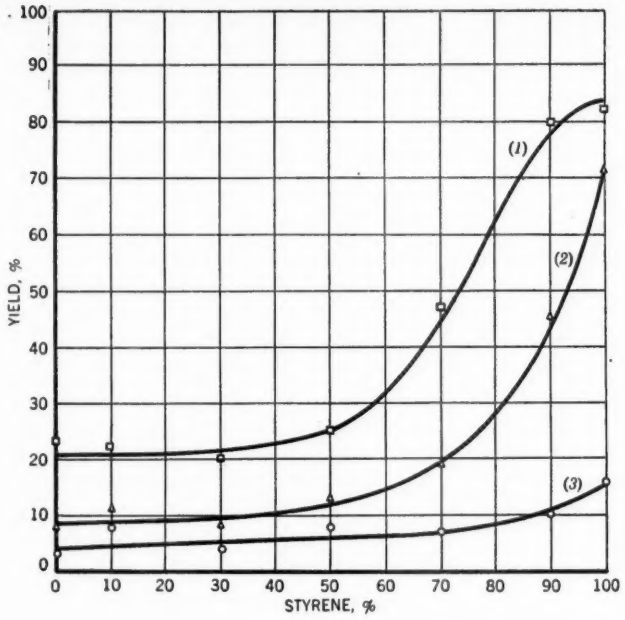

FIG. 5.

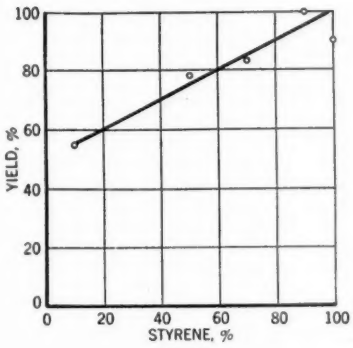

FIG. 6.

FIG. 4.—Yield as a function of reaction time at 50° C. Typical mixture for the preparation of Buna-S: 7.5 parts butadiene, 2.5 parts styrene (by weight), 3 parts of the mixture, 7 parts 10% sodium oleate solution (by volume), 0.5% ammonium persulfate (calc. on monomeric mixture); shaking machine, 110 turns per minute.

FIG. 5.—Yield as a function of styrene content in mixtures of butadiene and styrene at 50° C. 3 parts of the mixture, 7 parts 5% ammonium linoleate solution (by volume), 0.5% ammonium persulfate (calculated on monomeric mixture); shaking machine, 60 turns per minute: (1) after 4 hours; (2) after 7 hours; (3) after 17 hours.

FIG. 6.—Yield as a function of styrene content in mixtures of butadiene and styrene at 20° C. Reaction time, 70 days (=1,680 hours); other experimental conditions correspond to those of Figure 5.

As may be noted from Figure 5, the rate is influenced only by high concentrations of styrene; the same is true for the reactions at room temperature (see Figure 6).

Although these results were quite satisfactory, still more suitable condi-

tions were finally evaluated. Using 1 per cent of the catalyst and sodium linoleate at 50° C, yields of 70–80 per cent were obtained after about a day.

Butadiene–Acrylonitrile.—The yield–time curve for one mixture, given in Figure 7, suggests that the situation is more complicated. The nitrogen con-

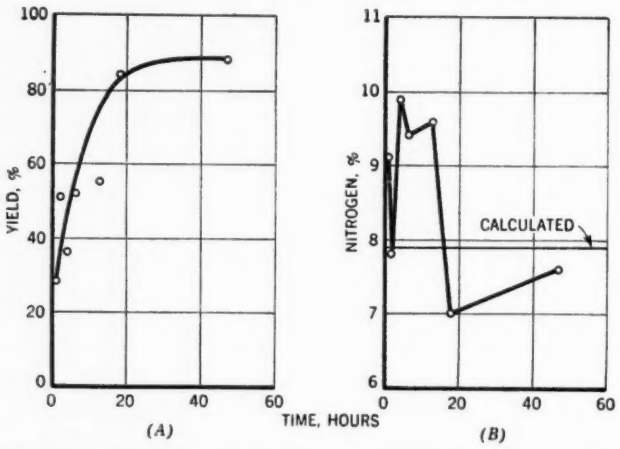

FIG. 7.—Yield (*A*) and percentage nitrogen (*B*) of the corresponding copolymers as a function of reaction time at 50°C. Typical mixture for the preparation of Perbunan: 7 parts butadiene, 3 parts acrylonitrile (by weight), 3 parts of the mixture, 7 parts 5% sodium oleate solution (by volume), 0.5% ammonium persulfate (calculated on monomeric mixture); shaking machine, 60 turns per minute.

tent indicates fluctuations in the composition of the polymers during synthesis. One may conclude, from such irregularities, that no simple formula can describe the actual structure of the copolymers.

Reference has already been made to the particular behavior of acrylonitrile in emulsion. As may be seen from Figure 8, small quantities of butadiene are

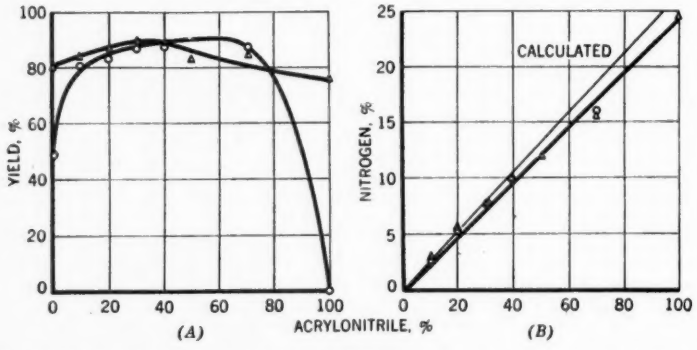

FIG. 8.—Yield (*A*) and percentage nitrogen (*B*) of the corresponding copolymers as a function of acrylonitrile content in mixtures of butadiene and acrylonitrile at 50° C. 3 parts of the mixture, 7 parts 5% sodium oleate solution (alkaline emulsion) or of 5% Fixanol solution (acid emulsion) (by volume), 0.5% ammonium persulfate (calculated on monomeric mixture); reaction time, 18 hours; shaking machine, 60 turns per minute: (○), sodium oleate; (△), Fixanol.

sufficient to accelerate the polymerization of the nitrile; on the other hand, the presence of some nitrile also accelerates the reaction of butadiene. As a result, a maximum in yield as a function of the nitrile concentration has been

observed. Since Fixanol has a favorable influence on the reaction of the pure nitrile, the same maximum is less pronounced in acid emulsions. The polymers isolated contain less nitrogen than corresponds to the monomeric mixtures, but on the whole the increase in nitrogen content is regular.

The temperature function for the formation of copolymers is exceedingly small and similar yields are, therefore, obtained (after about the same time) between 50° and 35° C. Even at room temperature the reactions are completed within a few days.

Dimethylbutadiene–Acrylonitrile.—The kinetic picture for the production of this new class of copolymers is the same as in Figure 8. The maximum rate is, however, still more pronounced, as may be seen from Figure 9.

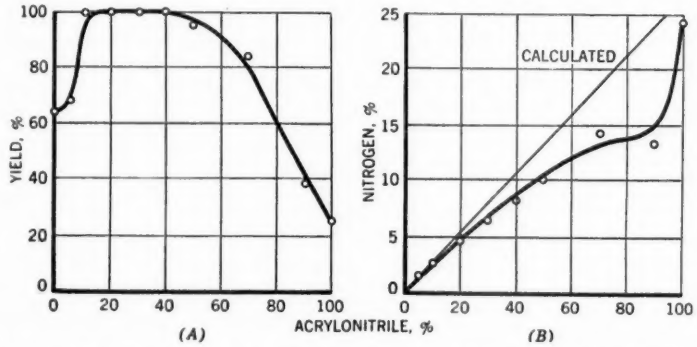

FIG. 9.—Yield (*A*) and percentage nitrogen (*B*) of the corresponding copolymers as a function of acrylonitrile content in mixtures of dimethylbutadiene and acrylonitrile at 50° C. 3 parts of the mixture, 7 parts 5% sodium oleate solution (by volume), 0.5% ammonium persulfate (calculated on monomeric mixture); reaction time, 18 hours; shaking machine, 60 turns per minute.

The physical properties of these copolymers are very unexpected, and will be discussed in the following section. Although the rate of dimerization is very small at moderate temperatures, all polymers possess the distinct smell of the cyclic dimers formed by the Diels-Alder reaction of the diene and acrylonitrile[1].

SOME PROPERTIES OF COPOLYMERS

ELEMENTARY COMPOSITION

Nonhydrocarbon Components.—Technical Buna-S has been analyzed by Nowak[13]; we can confirm his results. When extracted with acetone, 7–10 per cent of the material is dissolved; a small part of the soluble fraction consists of polymers; linoleic acid is the main product. The corresponding copolymers prepared in our laboratory were also contaminated with 5–7 per cent of linoleic acid or (in other experiments) oleic acid, while 5–20 per cent of the polymers—depending on the reaction time—were still soluble in acetone.

The emulsifying agent from Perbunan was extracted with water, as the polymer is partly soluble in acetone. The water extract was concentrated and the organic material taken up in methanol. It contained the antioxidant and a sulfonic acid, probably isopropylnaphthalenesulfonic acid. As the corresponding copolymers were prepared with other emulsifying agents, it is evident that the nature of the latter is not of primary importance for the preparation of copolymers.

Elementary Analysis.—The elementary analysis of copolymers from styrene gives some idea about the influence of oxidation during preparation of the polymers. Technical Buna-S had the following composition after extraction with acetone:

C(%)	H(%)	Ash (%)	O(%) (difference from 100%)
88.4	10.4	0.8	0.4
85.8	10.0	0.6	3.6

The oxygen content, especially high in the second case, indicates either that oxidation has taken place or that a part of the linoleic acid has become insoluble and interlinked with the polymers.

Similar results were obtained with polymers prepared in our laboratory; the following data refer to products isolated after 70 per cent yield had been obtained:

Styrene (% in monomeric mixture)	Styrene (% in copolymer calculated from analysis)	C(%)	H(%)	O(%) (difference from 100%)
30	23	84.3	9.8	5.9
50	40	87.9	9.5	2.6
70	53	88.1	9.0	2.9

These figures indicate that the concentration of styrene in the polymer is probably lower than in the original mixture.

Similar results have been found with nitrile copolymers (see Figure 8). Technical Perbunan had the following composition after removal of the water-soluble substances.

	C(%)	H(%)	N(%)	Ash (%)	O(%) (difference from 100%)
Perbunan	82.0	9.5	6.7	0.6	1.2
Perbunan Extra	80.7	8.9	8.6	1.0	0.8

According to these figures, Perbunan contains one nitrile group for 12–13 carbon atoms, while Perbunan Extra has about one nitrile group for 9–10 carbon atoms.

Fractionated precipitation by means of alcohol does not lead to fractions with different nitrogen contents. This, however, is not an exact proof of the regular structure of these copolymers, because in our own experiments we encountered products with fluctuating nitrogen content after synthesis, as illustrated by Figure 7, which indicates an irregular structure for technical products.

Unsaturation.—The determination of the double bond content, following a slightly modified procedure for natural rubber (iodine chloride, carbon tetrachloride), is disturbed by side reactions. Such side reactions are much more pronounced with dimethylbutadiene derivatives than with butadiene derivatives and it is assumed that, in the first case, more substitution occurs. Figure 10 gives a semiquantitative picture of the changes observed with increasing quantities of nitrogen in the polymers. Both polymers from the pure dienes show 25 per cent loss of unsaturation. The incorporation of nitrile has a favorable effect on the butadiene copolymers but only little influence on the products containing dimethylbutadiene. Such differences as illustrated by Figure 10 may have much bearing on the mechanical properties of the copolymers.

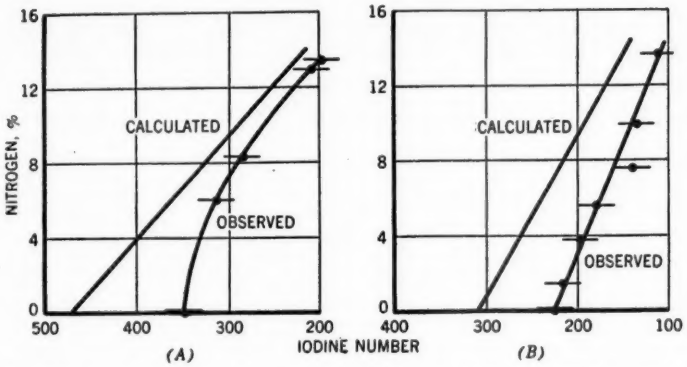

FIG. 10.—Calculated and observed unsaturation (iodine number) of nitrile-diene copolymers as a function of percentage nitrogen. Limits of experimental error are given by ●. (*A*) butadiene series; (*B*) dimethylbutadiene series.

INTERACTION WITH SOLVENTS, MECHANICAL PROPERTIES, AND SOME EXPERIMENTAL DATA

Solubility.—The solubility of diene polymers is a function of the reaction time. At yields of about 70 per cent, polybutadiene becomes practically insoluble. The addition of styrene leads to a gradually increasing quantity of a soluble fraction. Copolymers with acrylonitrile exhibit the same properties; with higher nitrile concentration, however, the exceptionally strong association caused by the nitrile groups again diminishes the solubility of the polymers; no accurate conclusions about the three-dimensional structure of these polymers are, therefore, possible.

Polymers from dimethylbutadiene have a very different character. Methyl rubber itself is much more soluble than polybutadiene, even at higher yields, and can be easily broken down on the mill. Copolymerization with acrylonitrile tends to increase the solubility and solutions can be prepared from the copolymers. The significant influence of small quantities of nitrile groups can thus be demonstrated by precipitation of the polymers from their chloroform solution with saturated hydrocarbons. Figure 11 may serve as an example.

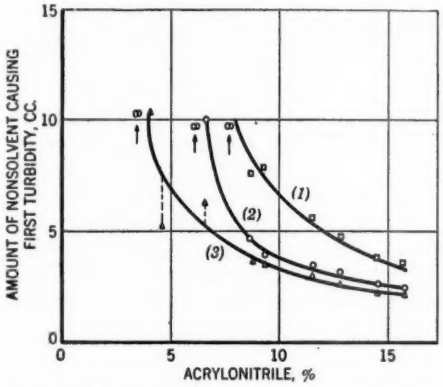

FIG. 11.—Influence of acrylonitrile content on solubility of copolymers from dimethylbutadiene and acrylonitrile at 25° C. Solutions of 1 g. copolymer in 100 cc. chloroform. Nonsolvents: cyclohexane (1), hexane (2), pentane(3).

As may be seen from Figure 11, the solvent power increases in the expected order: pentane < hexane < cyclohexane. Using toluene as a solvent of minor solvent power and pentane as a nonsolvent, polymers with only 2 per cent nitrogen, corresponding to one nitrile group for about 49 carbon atoms, precipitate.

The influence of concentration of the polymer in the ternary system: solvent–polymer–nonsolvent has been treated theoretically by Brønsted[14], Huggins[15], and Schulz[16]. According to the latter, the following empirical equation describes the results, when the temperature is kept constant:

$$\gamma = \frac{a - \ln c}{b}$$

In this formula γ represents the ratio of the volume of nonsolvent to the total volume, at the point at which a turbidity becomes just visible; a and b are empirical constants related to the degree of polymerization and to the interaction of the three components.

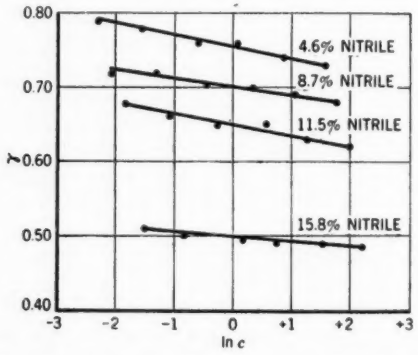

FIG. 12.—Influence of concentration on solubility (expressed by γ) of copolymers from dimethylbutadiene and acrylonitrile at 25° C. Varying acrylonitrile contents. Solvents, chloroform; nonsolvent, hexane.

As it was thought possible that γ might change in a typical way with percentage nitrogen, some measurements were made, varying the concentration of the polymers from 0.1–15 g. per liter. The results are given in Figure 12.

Our results are in agreement with the equation of Schulz, but no simple relation seems to exist between the slope of the lines and the nitrogen content of the copolymers. This may be due to differences in the distribution functions of molecular weights, which can counterbalance the effect of nitrile groups on γ.

Swelling.—Although the change in swelling properties of styrene copolymers is a very gradual one, we found a more pronounced influence of the nitrile groups. On the whole, a comparison of vulcanized samples is more typical, since small variations inherent in the raw material are flattened out. But even in comparatively strong swelling agents, such as toluene and carbon tetrachloride, the influence of the nitrile group remains predominant, as may be seen from Figure 13.

The swelling is given in weight fractions (ratio of the weight of swelling agent to the weight of swelling agent minus weight of polymer). The degree of swelling in chloroform is an approximate measure of the amount of cross-

linking in copolymers with a low nitrile content. If the latter increases (from about 15 per cent upward), the strong dipole interaction of the nitrile groups becomes predominant. A very striking picture of this phenomenon may be seen in Figure 13 *B*, where, especially in the cases of the weaker solvents, carbon tetrachloride and toluene, the very steep slope of the curves indicates a sudden transition from totally soluble to moderately swelling materials as a consequence of a relatively slight increase of nitrile content. Chloroform remains a good swelling agent, as is also the case with butadiene copolymers (Figure 13 *A*). But here the effect of cross linking is coöperating with the dipole interaction; hence, the more gradual decrease in swelling power.

Mechanical Properties and Structural Units.—As has been stated in the previous paper, copolymers from dimethylbutadiene differ fundamentally from those of butadiene.

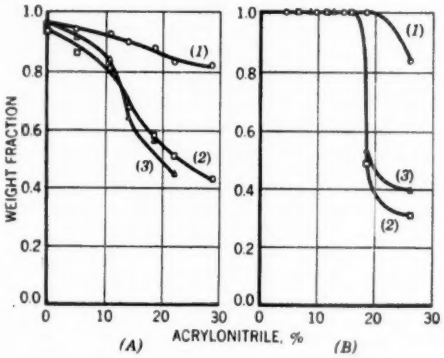

FIG. 13.—Influence of acrylonitrile content on swelling equilibrium of copolymers (expressed in weight fractions) at 25° C: (*A*) butadiene series; (*B*) dimethylbutadiene series. Solvents: chloroform (1), toluene (2), carbon tetrachloride (3).

A few nitrile groups are sufficient to transform methyl rubber to a thermoplastic material resembling gutta-percha. With more nitrile groups the temperature of elasticity approaches 100° C. A vulcanized sample, corresponding to Perbunan Extra in nitrogen content, becomes extensible and elastic in boiling water, but hardens as soon as it is removed from the bath. We shall describe quantitative experiments in the fifth paper of this series but we now will discuss some possible structural causes of this remarkable phenomenon.

The following differences can be deduced from the previous experiments:

Structural units	Perbunan	Dimethyl Perbunan
Methyl groups	None	Two
1,2:1,4 addition	?	?
Cyclization	Little	Much
Cross linking	Moderate	None

The only obvious difference between the two groups of polymers is the proportion of cyclo groups in the dimethyl derivatives. As is known from the cyclization of natural rubber, such cyclo groups in the macromolecular chain tend to increase the temperature of elasticity; so it is conceivable that the combination of cyclo, methyl, and nitrile groups leads to an exceptionally high temperature of elasticity.

Some Experimental Data.—The monomers used were of the same quality as described in the previous papers. The soaps used were only of commercial

purity, but the same sample was used throughout the investigation. Polymerization was carried out in sealed test-tubes, with only a small volume of air left in the tube. This may account for the fact that inhibition by air, as has been described by other investigators, has not been observed in our experiments with styrene. The tubes were shaken horizontally in small air-heated thermostats mounted on ordinary laboratory shaking machines. Duplication of experiments at high yields (70–100 per cent) was usually satisfactory. The latex was coagulated with methanol or an alcoholic solution of sodium chloride. After thorough washing with alcohol, we dried our samples on a laboratory rubber mill (Thropp type).

SUMMARY

The copolymerization in emulsion of butadiene with varying proportions of styrene and acrylonitrile and of dimethylbutadiene with the latter vinyl compound was studied on a laboratory scale. An essential difference between polymeric vinyl compounds and polydienes is the olefinic character of the latter, which leads to typical secondary changes in the polymers originally formed during the completion of the reaction. Such changes are of fundamental importance for the ultimate mechanical properties of polymers and copolymers based on dienes. After a brief discussion of the general theoretical line of thought serving as a base for our experiments, the influence of various factors on the rate of polymerization is pointed out and demonstrated by experiments. The changes in the nitrogen content of copolymers from acrylonitrile and the yields as a function of the reaction time also were studied. From an investigation of some physical properties, such as solubility and swelling, the existence of true copolymers (of unknown irregularity) is established. Copolymers from dimethylbutadiene and acrylonitrile represent a new class of olefinic thermoplastics resembling gutta-percha.

ACKNOWLEDGMENT

The authors wish to thank W. Gaade for the performance of some experiments and J. W. F. van't Wout for his valuable assistance.

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THE STATE OF POLYDISPERSION OF HEVEA LATEX. II.*

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THE RELATION BETWEEN THE SIZE OF LATEX PARTICLES AND THE PROPERTIES OF THE RUBBER HYDROCARBON

The rubber hydrocarbon present in crude rubber is composed of a polymolecular mixture of filiform molecules, which, according to the concept of Kuhn, are to be regarded as easily deformable spherical units and not as small rigid rods. The polymolecular state of rubber, which is a general characteristic of macromolecular substances, is manifest only when the rubber is fractionated, for, when applied to unfractionated rubber, ordinary methods of analysis give only the mean molecular weight, in other words, the mean degree of polymerization.

By fractional solution of rubber in hexane, Kemp and Peters[1] obtained a series of fractions, the molecular weights of which increased progressively with the time of treatment.

In the present work, the purpose was to determine whether, in the fractionation of latex into particles of different sizes, there is a corresponding separation of the rubber hydrocarbon into fractions of different molecular sizes. With this in view, the viscosity, plasticity, gel rubber constant, and permanent deformation of each of the samples of rubber which had been obtained in the earlier part of the work were determined.

The viscosity law of Staudinger makes use of the factor η_{sp}/c, where η_{sp} is the specific viscosity, and c is the concentration of the dissolved substance (in grams per liter). Although, in the case of rubber, this factor is not strictly proportional to the degree of polymerization, its determination for the various fractions for different molecular weights does give useful information.

The plasticity was measured by a Hoekstra balance plastometer[2] at a temperature of 70° C. It is expressed by the D_{30} value, *i.e.*, the thickness of the test-specimen (in mm.) after the load has been applied for 30 minutes. These values are a function of the length of the filiform molecules of crude rubber, but must not be assumed to be proportional to the molecular weight.

The content of insoluble rubber (gel rubber) was determined by treating finely divided samples of rubber with benzene three times for twenty hours each in darkness. The results were comparable to those obtained by the viscosity measurements. The fact that rubber does not entirely dissolve points to the presence of large macromolecules which form a true three-dimensional network. This network is, moreover, not formed merely by primary bonds, since it has been shown that the solubility of rubber also depends, in large measure, on

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 21 No. 9, pages 177–180, September 1944. Part I was published in the *Revue Générale du Caoutchouc*, Vol. 21, No. 8, pages 155–160, August 1944, and reprinted in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 19, No. 1, pages 176–186, January 1946. Eleven bibliography references were omitted in Part I, but now appear in the bibliography at the end of the present paper.

secondary bonds[3]. According to the literature, the percentage of gel reaches 20 to 40 per cent, and depends, among other factors, on the nature of the solvent and the time that the solvent acts on the rubber. Kemp and Peters[1], in a study of well preserved latex, obtained a value of approximately 90 per cent, and concluded from their experiments that rubber hydrocarbon is originally present in the form of gel rubber in latex, and that this gel rubber is subsequently transformed into sol rubber by oxidation. We do not agree with this view because, according to the data of Kemp and Peters, dissolution in hexane under the conditions indicated was definitely not complete at the end of 72 hours, and it is possible that the low solubility observed is attributable to the intensive preliminary drying over phosphorus pentoxide[4].

According to investigations by Soudijn[5], the permanent deformation shown by plasticized crude rubber after it has been stretched depends wholly on the time of plasticization and, under otherwise comparable conditions, the permanent set is related directly to the length of the chain molecules. Actually, however, this permanent deformation is influenced also by the presence or absence of a network structure. The measurements were made on small strips of rubber maintained at 20° C for 24 hours at an elongation of 200 per cent. All internal stresses in the rubber were eliminated after the rubber was released from stretching by placing the samples in a mixture of benzene and alcohol[6], and then measuring the permanent deformation.

For these tests, samples of rubber were prepared, on the one hand, by evaporation or coagulation of unpurified latex; on the other hand, from latex purified by dialysis and precipitation. The compositions are shown in Tables 2 and 4 of the previous work[7]. During the preparation and treatment of the samples, any heating and prolonged exposure to daylight were avoided, but no attempt was made to exclude any of the effects which might result from exposure to air. Actually in the case of samples of purified rubber, slight degradation by oxidation was noticeable. In the case of unpurified rubbers, the high contents of nonrubber components and differences in composition of the various samples had an influence on the experimental results. In all the tests, however, these causes of error were reduced to a minimum.

Figure 1, which summarizes the results obtained, shows that there is a close relation between the properties of the rubber hydrocarbon and the diameter of the particles. It is evident from the trend of the curves representing the relation between the plasticity D_{30} and the η_{sp}/c factor on the one hand and the diameter on the other, that the degree of polymerization of the rubber molecules decreases with decrease in the size of the particles. The change in permanent deformation showed a similar functional relation.

The separation of latex into fractions of decreasing particle size gives, then, a series of rubbers the molecular sizes of which likewise decrease. It would be expected, as a result, that a latex globule is composed of a mixture of different molecules, the mean degree of polymerization of which is a function of the diameter.

When crude rubber is masticated for increasing lengths of time, a series of products is obtained, the molecular sizes of which decrease progressively. Because of the close analogy between the results obtained by two such different methods, it was of interest to compare these results. Figure 2 shows the results obtained with a series of crepe rubbers which were masticated for increasing lengths of time on a laboratory mill, the roll temperature of which was 80° C. By comparing Figures 1 and 2, it will be seen that the respective values

of η_{sp}/c and D_{30} are practically the same for crepe masticated 30 minutes and for the corresponding rubber the particles of which are 0.15μ, *i.e.*, fraction (8 + 9). However, this analogy does not apply to the permanent deformation nor to the gel rubber content. These last properties change in a regular way as functions of the size of the latex particles, and the highly plasticized rubber of fraction (8 + 9) still had a gel content of approximately 20 per cent and a permanent deformation of 40 per cent. On the contrary, even after a very brief time of mastication, the rubber became entirely soluble and its permanent deformation increased greatly.

This shows that the rubber of fraction (8 + 9) and crepe plasticized 30 minutes did not have the same structures, in spite of the fact that their filiform molecules were of practically the same length. There must have been present in the former a molecular network which resulted in only partial solubility and a small permanent deformation, whereas in the case of plasticized crepe, mastication destroyed completely the network structure originally present.

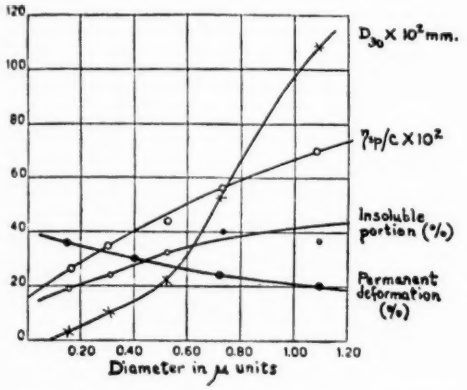

FIG. 1.—Relations between some properties of rubber hydrocarbon and the mean diameter of the latex particles.

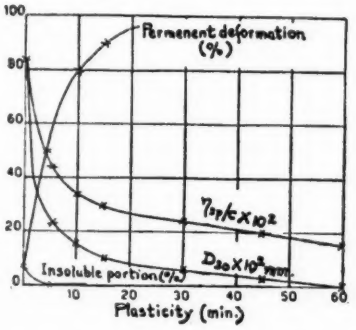

FIG. 2.—Influence of plasticization on the properties of rubber hydrocarbon.

With respect to the fractionation experiments of Kemp and Peters[1], which have already been mentioned, it should be noted that the values of η_{sp}/c are in the ratio of 1:3.5 for the fractions containing the smallest and the largest particles. In the experiments which are to be described, this ratio is only 1:2.5. It would be expected that, in view of the more extended fractionation of latex into monodispersed fractions and the complete absence of oxygen in the operations, these methods would make possible a very exact analysis of the rubber hydrocarbon.

THE RELATION BETWEEN THE SIZE OF LATEX PARTICLES AND THE DEGREE OF POLYMERIZATION WITH RESPECT TO THE BIOSYNTHESIS OF RUBBER

To explain the relation between particle size and degree of polymerization, it might be assumed that, in fresh latex, the mean molecular size of the rubber particles is almost the same in all the globules, but that oxidation ultimately causes more advanced degradation of the small particles than of the large particles.

However, investigations by de Vries[8] have shown that the rubber hydrocarbon changes to only a very slight extent in latex which has been preserved with ammonia for several years. This is at variance with the hypothesis above. Other observations likewise indicate that, in the case of fresh latex, there is a relation between particle size and degree of polymerization. As an example, work at the Buitenzorg Proefstation in West Java from 1920 to 1930 showed on the one hand that latex from young trees, or when tapping has been severe or delayed, contains chiefly small particles[9]; but, on the other hand, that rubber prepared from latex of these types is much more plastic and has a lower viscosity than latex from trees tapped under normal conditions[10]. A comparison of these independent observations leads to the conclusion that there is a relation between particle size and degree of polymerization.

In attempting to explain this relation, it will be helpful to examine critically the various hypotheses on the biosynthesis of rubber. Some of these are based on the assumption that the rubber hydrocarbon is present in the liquid state and in a low degree of polymerization in the tree, and that at a definite time the degree of polymerization increases, starting at the surface of the particles and progressing into the interior[11]. Other hypotheses are based on the view that the formation of macromolecules in nature probably involves equilibrium reactions rather chain reactions[12], in which case rubber hydrocarbon is formed directly in a high molecular state in the tree.

Although there is still no experimental evidence to prove this view, the first hypothesis seems to be the more probable one. It is important to note in this connection that an analogous type of reaction has been described in the literature of polymerization reactions, *i.e.*, the "bead polymerization", in which polymerization is carried out in droplets of dispersed monomer[13]. Furthermore, this point of view is in best accord with the results of various investigations, and several arguments are to be found in favor of the presence of rubber in a state of low polymerization in the tree.

The first point is the nonspherical form of the rubber particles. Frey-Wyssling[14] assumed that rubber particles are formed by the intermediary action of plastides, *i.e.*, certain components of protoplasm, and are pear-shaped as a result of their unilateral growth. This is not very probable, because a microscopic study of latices of different rubber plants[15] has shown that their rubber particles are formed directly as globules in the protoplasm. The fact that they are not spherical ought rather to be explained on the basis that the product is originally a liquid in a relatively low state of polymerization. When a rubber tree is tapped, there is, in a short time, a flow of several hundred cubic centimeters of latex from a very extensive system of laticiferous vessels, and because of the rapidity of this flow, the globules tend to acquire an ellipsoidal form[16]. The presence of asymmetrical particles, with a tail, or pear-shape, may be accounted for by the passage of large viscous globules through narrow orifices. In the vascular system of Hevea, there are innumerable constrictions[17], which connect the laticiferous vessels to one another, and also, in the sclerenchymatic tissue, external rows of degenerate vessels in which very large latex particles may form. It is possible that this asymmetry is then fixed by polymerization, which commences on the surface of the particles after flow of the latex. As to what substances act as catalysts, there is as yet no explanation. Two patents[18] may, however, be mentioned, which recommend the use, in polymerizing dienes, of certain enzymes isolated from latex or from the cortex of Hevea. Furthermore, consideration must be given to the influence of

oxygen, which perhaps acts in conjunction with light during the flow of the droplets of latex from the location of tapping to the receiving cup.

A second point to be considered is the fact that Freundlich and Hauser[19], as the result of a study by means of a micromanipulator of the structure of rubber particles in freshly collected latex, concluded that the particles are composed of viscous substances enveloped in an elastic coating of gel rubber. This is in accord with the view that the polymerization of a substance which initially is only slightly polymerized begins on the surface of the particles.

Still another fact to be considered is that the microscopic examination of latex from various rubber plants, including Ficus elastica, Castilloa elastica, jelutong and Manihot glaziovii, has shown that rubber particles are present as a more or less viscous liquid. Likewise, from experiments on fresh Castilloa latex, Weber[21] concluded that the rubber globules are viscous and that elastic rubber is formed by subsequent polymerization only after drying or coagulation. However, in view of the fact that only in the last few years has there been any extended study of the mechanism of polymerization reactions, it would seem desirable to repeat the experiments of Weber.

Finally the relation between the size of the particles and the degree of polymerization can likewise be explained by the mechanism of bead polymerization. It is known, as the result of numerous investigations, notably those of Schulz and Husemann[22], that, in a polymerization reaction, the length of the chains depends in large measure on the rate of the reaction. At elevated temperatures or with a very active catalyst, the rate of the reaction is high, and to a great extent short chains are formed, whereas if the reaction is slow, long chains are formed. As a consequence, if polymerization commences at the surface of the rubber particles under the influence of a catalyst in solution in the serum, it may be assumed that the rate of polymerization of small particles, which have a larger surface area than that of an equal volume of large particles, is greater and the resulting chains are shorter.

Accordingly, if it is accepted that globules of various diameters are formed in the protoplasm of the laticiferous vessels of Hevea brasiliensis, and that the hydrocarbon of which they are composed, originally of low molecular weight, forms long molecules only after tapping and as a result of polymerization commencing at the surface of the globules, then it is possible to explain certain observations and to establish relations between them. It is, of course, well understood that this hypothesis is subject to experimental verification; nevertheless, it should, even as things stand, be of some service.

POSSIBILITIES IN THE PRACTICAL APPLICATION OF DISPERSOIDAL ANALYSIS TO HEVEA LATEX

We shall limit ourselves to a brief discussion of certain possible applications of dispersoidal analysis to Hevea latex, while reserving for a later publication the details of its practical utilization.

EVALUATION OF A PARTICULAR SYSTEM OF TAPPING

The best system of tapping for a given type of rubber plant is determined by systematic measurements in production and by practical experiments over long periods. It is therefore, advisable to make use of a more rapid method and one which involves fewer operations. It would appear that this can be accomplished by periodic determinations of distribution curves of latex, since it is known that the diameter of rubber particles decreases when tapping is severe[8].

SELECTION OF PLANTATION MATERIAL ACCORDING TO ITS SPECIAL TECHNOLOGICAL CHARACTERISTICS

It is known that rubber from certain clones is particularly plastic[22], but it is not known whether this is to be attributed to the small diameters of the particles of these latices. A study of this problem, involving dispersoidal analyses and systematic plasticity measurements, should prove itself to be of considerable importance.

There is still another point in connection with which the determination of distribution curves of different latices might be of interest. In the plantation rubber industry, it has been found that certain latices, particularly those obtained from selected young trees, offer serious difficulties in the preparation of concentrated latex, whether this is prepared by creaming, by centrifugation or by evaporation, difficulties which are evident, for example, in the high losses of rubber in the serum and by the high viscosity of the concentrated latex. These anomalies are probably attributable, to an important degree, to the high content of small particles in these latices. It should be possible to settle this point by a special investigation.

PREPARATION OF LATEX AND OF CRUDE RUBBER WITH SPECIAL PROPERTIES

The fractionation of rubber latex according to the size of its particles makes it possible to obtain products with widely different compositions and properties. The fractions in which large particles predominate yield concentrated latex, the degree of purity of which is high, and which is satisfactory when a rubber having low water absorptive capacity is desired. Coagulation of this latex yields a rubber which is relatively pure and has a low protein content.

As for the fractions which contain predominantly small particles, they lend themselves principally, when purified and concentrated, to the impregnation of fibers and textiles; on the other hand, by coagulation they yield plastic rubber.

CONCLUSIONS

The influence of the degree of dispersion in latex on the composition and properties of the rubber was studied in detail by means of a series of latices, the mean particle size of which ranged from 1.1 to 0.15μ in diameter. These fractions were first obtained by centrifugation of preserved latex, and the degree of distribution was measured by photomicrographic analysis and by sedimentation.

This method of fractionation yields latices and rubbers with compositions which differ widely. With decrease in the size of the particles, their surface area per unit of rubber increases, and the percentage of nonrubber components which is adsorbed irreversibly or which is dissolved in the serum increases greatly.

On the contrary, the degree of polymerization decreases with decrease in the diameter of the particles. This may be explained by the fact that, in the beginning, the polymerization of the globules is relatively low, and that it progresses under the influence of a catalyst present in the serum. In brief, then, systematic dispersoidal analysis of Hevea latex is of prime importance in the plantation rubber industry.

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THE THERMOELASTIC PROPERTIES OF RUBBER *

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In an earlier communication, Meyer, von Susich and Valkó[1] showed that within certain limits of extension (100 to 300 per cent) and at constant elongation, the stress in a rubber sample is proportional to the absolute temperature. Within these limits, the stress is therefore analogous to the pressure of an ideal gas, which at constant volume is likewise proportional to the absolute temperature. Such behavior of rubber or of any other rubberlike substances is said to be *ideal*.

However, a sample of rubber which exhibits ideal behavior at elongations of 100 per cent and higher deviates from this ideal behavior at elongations below 100 per cent and greater than 500 per cent. One of the reasons for such deviations at high elongations has already been discussed in an earlier publication[2]. As a result of extension, rubber tends to crystallize. The resulting crystallites do not contribute to the elastic stress, but if the temperature is raised, they fuse and thereby increase the tension, which then increases more rapidly than is the case with an ideal rubber.

Deviations from ideal behavior at small deformations have not yet been studied thoroughly, so it is these deviations which are the first subject of discussion in the present paper. First of all the experimental facts will be presented.

The thermal coefficient of the force F at constant elongation Δl, $(\partial F/\partial T)_{\Delta l}$, is negative at low elongations, *i.e.*, up to 10 per cent; in other words, the force decreases with increase in temperature, and the coefficient of linear expansion in the direction of the force remains positive, like that of an ideal material. At an elongation of approximately 10 per cent, the stress is independent of the temperature; at this point the coefficient of linear expansion in the direction of elongation is, therefore, equal to zero. At higher elongations, the stress increases with rise in temperature, an indication that the coefficient of linear expansion is negative.

On the other hand, if rubber is subjected to a force inverse to that of extention (by exerting pressure in only one direction), it will be found that the coefficient of linear expansion, $(\partial l/\partial T)_F$, remains positive. The pressure exerted by the rubber against this force increases at first very rapidly with rise in temperature when the deformation is still small. At greater deformations, the behavior tends toward the ideal.

THE THERMODYNAMICS OF ISOTHERMAL DEFORMATIONS

As a means of interpreting these phenomena on a molecular basis, it was decided first of all to derive thermodynamic equations for isothermal deformations. Heretofore changes in volume during elastic deformation have been

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Helvetica Chimica Acta*, Vol. 29, No. 7, pages 1842–1853 (1946).

disregarded, and materials have been treated as if they were incompressible[3]. However, unilateral compression certainly must involve an increase in pressure, at least in certain parts of the sample, and a tension force should have the opposite effect. An increase in pressure brings about a diminution in volume and, correspondingly, tension results in an increase in volume. The more compressible the material is, the greater is this effect.

It can be readily shown that, when stretched, rubber tends to increase in volume. A cylindrical tube of vulcanized rubber, placed horizontally, is filled with water; it is closed at one end, and a glass capillary tube is inserted at the other end. When the tube is stretched, water is drawn from the capillary tube; hence, the internal volume of the tube has increased[4]. If the water inside the tube is replaced by rubber, the volume of the latter must increase likewise, although to a much less extent. This phenomenon will be taken into account in the discussion to follow.

Part of the work expended on rubber by stretching is, then, absorbed as work of changing the volume against the external pressure, *e.g.*, against atmospheric pressure. If, at temperature T, constant pressure P, and tension force F, a sample of rubber is deformed (stretched) an infinitesimal amount, dl, the work expended on the rubber is $F \cdot dl$. This work is equal to the sum of the changes in energy and of the product, $-TS$ (where S is the entropy), plus the work of changing the volume against the pressure, $P \cdot dV$:

$$F \cdot dl = dE - T \cdot dS + P \cdot dV \tag{1}$$

For a transformation at constant temperature and constant pressure, the following relation holds true:

$$F = \left(\frac{\partial E}{\partial l}\right)_{T,P} - T\left(\frac{\partial S}{\partial l}\right)_{T,P} + P\left(\frac{\partial V}{\partial l}\right)_{T,P} \tag{2}$$

Maintaining the length l and the pressure P constant, the derivative with respect to T is:

$$\left(\frac{\partial F}{\partial T}\right)_{l,P} = \left[\frac{\partial^2 E}{\partial T \cdot \partial l} - T\frac{\partial^2 S}{\partial T \cdot \partial l}\right] - \frac{\partial S}{\partial l} + P\frac{\partial^2 V}{\partial T \cdot \partial l} \tag{3}$$

The term within the brackets can be written:

$$\frac{\partial}{\partial l}\left[\frac{\partial E}{\partial T} - T\frac{\partial S}{\partial T}\right] \tag{3a}$$

If l and P are constant, $dl = 0$ and $dP = 0$, and Equation (1) becomes:

$$0 = dE - TdS + PdV$$

from which, assuming l and P to be constant:

$$\left(\frac{\partial E}{\partial T}\right)_{l,P} - T\left(\frac{\partial S}{\partial T}\right)_{l,P} + P\left(\frac{\partial V}{\partial T}\right)_{l,P} = 0$$

so that the term within the brackets in (3a) reduces to:

$$-\frac{\partial}{\partial l}P\frac{\partial V}{\partial T} = -P \cdot \frac{\partial^2 V}{\partial l \cdot \partial T} \tag{3b}$$

Thus Equation (3) becomes:

$$\left(\frac{\partial F}{\partial T}\right)_{l,P} = -\left(\frac{\partial S}{\partial l}\right)_{P,T} \tag{4}$$

Then substituting in Equation (2), the expressions (3b) and (4), there is obtained:

$$F = \left(\frac{\partial E}{\partial T}\right)_{T,P} + T\left(\frac{\partial F}{\partial T}\right)_{l,P} + P\left(\frac{\partial V}{\partial l}\right)_{T,P} \tag{5}$$

Accordingly the same equation is obtained as that of Elliott and Lippmann[5]. These authors call attention to the fact that, for an infinitely small pressure, the equation reduces to that derived by Wiegand and Snyder[6], and independently by Meyer and Ferri[2]. But this is true if $\partial v/\partial l = 0$ whatever is the value of P, and it is this last approximation (the constancy of volume during isothermal deformation) which had been introduced in the calculations[7]. Within the scope of this approximate theory, a distinction between $(\partial E/\partial l)_{P,T}$ and $(\partial E/\partial l)_{V,T}$ is, therefore, hardly possible[8]. We are in agreement with these authors that there is no sound basis for applying the "correction" to the elastic force in the first work[2], and one of the objects of our work is to eliminate this correction. We shall not discuss the other conclusions of Elliott and Lippmann, in particular their equations no. 38 and no. 45, which do not appear to the present authors to be justified.

Let us now examine the numerical magnitude of the work of changing the volume compared to that of the work of elasticity. For rubber, the stretch modulus, ϵ, is approximately 10^7 dynes per sq. cm. The work necessary to stretch 1 cc. of rubber to twice its original length is, therefore, approximately 5×10^6 ergs. With a compressibility[9] of 5.1×10^{-11} sq. cm. per dyne, a decrease in the hydrostatic pressure of 10^7 dynes per sq. cm. results in an increase in volume of 0.05 per cent. With a unilateral tension force of 10^7 dynes per sq. cm., an increase of the order of one-third of this value, *i.e.*, 0.02 per cent, would be expected. The work of changing the volume against the atmospheric pressure, *i.e.*, against approximately 10^6 dynes per sq. cm., is, therefore, 2×10^2 ergs. We have, then, as work expended, 5×10^6 ergs, of which the work of changing the volume ($P = 10^6$) is 2×10^2 ergs. Hence, for relatively low pressures, at least, the part of the total work involved in changing the volume can be disregarded.

This is true likewise of the surface work expended as a result of the increase in the surface against surface tension. The increase in the surface is 0.66 sq. cm., and is therefore an appreciable amount, but the surface tension is certainly less than 100 dynes per sq. cm., and the surface work is of the order of only several times 10 ergs.

The equations derived up to the present time can, therefore, be regarded only as approximations, but they are sufficiently close from the practical point of view. However, even if we can disregard numerically the change in volume with respect to the work expended, we cannot disregard it if it is desired to interpret the changes in internal energy or of entropy in terms of molecular statistics. Actually a very small isothermal change in the volume of rubber is accompanied by a considerable change in entropy and in internal energy. Scott[10] has determined the coefficient of cubic expansion, $(1/V)\cdot(\partial V/\partial T)$, of vulcanized rubber as 6.61×10^{-11} per degree, and the compressibility, $(1/V)\cdot(\partial V/\partial P)$, as -5.10×10^{-11} sq. cm. per dyne.

According to the general relations:

$$-\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P : \left(\frac{\partial V}{\partial P}\right)_T \qquad \text{and} \qquad \left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial S}{\partial V}\right)_T - P$$

there is obtained, when T is 300° K and the atmospheric pressure P is 10^6 dynes per sq. cm.:

$$\left(\frac{\partial S}{\partial V}\right)_T = 1.3 \times 10^7 \text{ ergs per cc.-degree, and}$$

$$\left(\frac{\partial E}{\partial V}\right)_T = 3.9 \times 10^9 \text{ ergs per cc.}$$

In the light of these values, rubber hardly differs in behavior from ordinary liquids. With the coefficients of expansion and compressibility recorded in the literature, the following values (when T is 300° K and P is 10^6 dynes per sq. cm.), for example, are obtained.

Liquid	$\left(\frac{\partial S}{\partial V}\right)_T$ in $\frac{\text{ergs}}{\text{cc.-degree}}$	$\left(\frac{\partial E}{\partial V}\right)_T$ in $\frac{\text{ergs}}{\text{cc.}}$
Benzene	1.65×10^7	490×10^7
Ether	1.33×10^7	400×10^7
Liquid paraffin	1.24×10^7	370×10^7
Rubber	1.3×10^7	390×10^7

The change in E for an increase in volume of 0.02 per cent is, then, 0.8×10^6 ergs per cc. for rubber, a value which is close to the same order of magnitude as the work expended in elongating the rubber 100 per cent. Even a still smaller change in volume, which would be difficult to measure, cannot therefore be disregarded.

STATISTICAL THEORY

It has been shown that, at medium elongations, rubber behaves almost like a perfectly ideal material. This means that the internal energy does not change, and that the free energy is practically equal to the product of the temperature and change in entropy. This is one way of expressing the probability, for the latter is diminished when the rubber is deformed, because the segments of the chain molecules orient themselves in a more orderly and, consequently, less probable arrangement.

Let us now consider lower elongations. Unquestionably these too lead to a more orderly geometric arrangement of the molecular segments, but experiments show that, instead of reducing the entropy, slight stretching increases it[11]. This increase may be attributed to the increase in volume brought about by the stretching. Accordingly changes in entropy are attributable to two superimposed causes, *viz.*, rearrangement of molecular segments and a change in volume. When the rubber is stretched only slightly, the second contributing factor is dominant and the entropy increases; when the elongation is about 10 per cent, the two causes compensate each other and there is no change in entropy. At still higher elongations the first contributing factor is dominant, so the result is a decrease in entropy.

A change in volume is manifest likewise when rubber undergoes unilateral compression. This type of deformation decreases the volume, and hence there is a decrease in entropy, which in this case is added to that resulting from the less irregular arrangement of the molecular segments. With a small uni-

lateral compression the entropy of rubber must, therefore, decrease more rapidly than that of an uncompressible rubberlike substance, and this conclusion agrees with experimentally observed facts.

In compression as in stretching the smaller the deformation, the more the volume effect masks the effect resulting from rearrangement of the molecular segments.

DEFORMATION BY SHEARING

The effects of changes in volume are clearly shown by comparing the results described above with the results when deformation involves simultaneous elongation and compression in such a way that the increase in volume resulting from elongation compensates for the decrease in volume resulting from compression. Under these conditions, the volume remains constant. This is the case in rotatory shearing, such as is realized in a rheometer (see Figure 1).

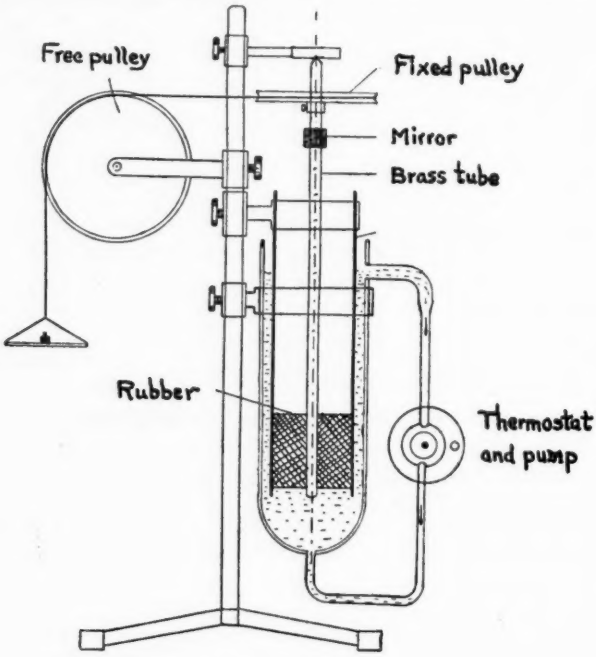

FIG. 1.

A cylindrical test-specimen of rubber is set in a rigid brass tube, with its entire lateral surface in contact. Through the rubber passes coaxially a cylindrical brass rod, at the top of which are a small mirror and a pulley. A torsion couple is exerted on the rubber by weights suspended by a wire which passes over a second freely turning pulley and then around the first pulley, which is attached rigidly to the vertical rod. The torsion couple C is measured by the product of the weight supported by the wire and the radius (35 mm.) of the fixed pulley. The torsion angle α is determined by means of a graduated scale placed one meter away and read, after reflection in the mirror, through a telescope.

The results of the measurements, the details of which are to be found in the "Experimental Part" of the present paper, are summarized in Table 1. $T/(\partial S/\partial \alpha)$ was calculated from the thermal coefficient of the couple, choosing very low values for the latter. Even with the largest couple, the angle of rotation was only two degrees. There was no question, then, that the experiments were carried out within a range of small deformations, *i.e.*, within a range in which deviations from ideal behavior are particularly evident when rubber is stretched. The last column of Table 1 gives the changes in free energy A as a function of the deformation, (*i.e.*, $(\partial A/\partial \alpha)_T$, calculated in the same units as those of the values in the other columns of Table 1. The numerical values refer to 1 gram of rubber.

TABLE 1

COMPARISON OF THE VALUES OF $-T \cdot \partial S/\partial \alpha$ AT DIFFERENT TEMPERATURES WITH THOSE OF $\partial A/\partial \alpha$ IN ERGS PER DEGREE OF ANGLE FOR ONE GRAM OF RUBBER

Force (g.)	Couple (dynes-cm.)	$-10^{-3}(\partial S/\partial \alpha)_T$ 20°	30°	40°	50°	60°	70°	$10^{-3}(\partial A/\partial \alpha)_T$
45	1.55×10^5	—	13	13	14	12	12	12
95	3.26×10^5	27	25	26	26	26	26	25
145	4.98×10^5	48	47	39	38	37	37	38

It is evident that the changes in free energy, $\partial A/\partial \alpha$, are equal to those of $-T(\partial S/\partial \alpha)$, and since at constant temperature:

$$\frac{\partial \alpha}{\partial A} = \frac{\partial E}{\partial \alpha} - T.\frac{\partial S}{\partial \alpha}$$

the change in internal energy is zero. The behavior of rubber is therefore virtually ideal, even at very small deformations provided these deformations are brought about by shearing stresses.

KINETIC THEORY

In this particular type of deformation, therefore, the effect of molecular rearrangement is quite clear. The elastic force originates solely in the thermal movements of the molecular segments; no change in the forces of attraction play any part in the phenomenon.

The considerable deviations from ideal behavior at low elongations can, therefore, be explained by a very small increase in volume of the rubber when it is subjected to a tractive force, an increase which escapes observation by ordinary methods. The increase in volume takes place among the molecular plane, and is characterized by a slight displacement of groups of atoms, *e.g.*, chain segments, which are displaced from their position of equilibrium. The expansion results in an increase in internal energy. Now it is known that the greater is this displacement from the position of equilibrium, the greater is the resistance against this displacement. Furthermore, as the elongation increases, the molecular chains orient themselves in the direction of the force, and this acts more and more on the primary valences. However, the latter are so rigid that displacement of the atoms continues to be extremely small and the increase in volume very slight. This is a second cause, of purely geometric origin, of the diminution of the factor $(\partial V/\partial l)$ when l increases. The two causes just cited act, then, in the same sense and account for the disappearance of the anomaly at medium elongations.

If there is crystallization, for example, at elongations of 200 to 400 per cent, the entropy decreases (liberation of heat of crystallization) and the internal energy does likewise. When the point of rupture is approached, *i.e.*, the point where the molecular chains are in a state of extensive orientation, the internal energy increases again, for then the external force, which has become relatively great, deforms the primary-valence angles, and this leads to an increase in energy and an increase in entropy as well.

Compression results in a decrease of energy and also in a decrease in entropy.

The changes in $(\partial E/\partial l)$ and $(\partial S/\partial l)$ are, then, very complicated because of the superimposing effects of several factors, including expansion against intermolecular forces of cohesion, elongation and orientation of the chain molecules, crystallization, and finally deformation of the primary-valence angles.

With respect to the first factor, it should be recalled that the forces of cohesion differ considerably according to the chemical nature of the rubberlike material; compare, for example, the forces of cohesion in apolar elastic hydrocarbons with those in keratin, the elastic ligament of hair, and with collagen, which are much greater because of the presence of hydrogen bonds. It is not surprising, then, that the change in internal energy as a function of the degree of elongation is by no means the same for all rubberlike substances. As a matter of fact, the behavior of copolymer of butadiene and styrene[12], GR-S, is quantitatively different from that of natural rubber. The difference for hair is still more pronounced, as has recently been shown by Woods[13]. However, in the opinion of the present authors, it would be wrong to draw, from these quantitative differences, the conclusion that the molecular phenomena during elongation of a hair are qualitatively different from those in rubber or in any other material with rubberlike elasticity. On the contrary it is felt that the long-range elasticity of keratin should not be attributed to a peculiar bending of the molecular chains under the influence of the forces of attraction, as assumed by Astbury, but that it is of the same nature as that of other typically rubberlike materials.

EXPERIMENTAL PART

In order to analyze the thermoelastic behavior of a substance, it is necessary to know the thermal coefficient of the deforming force under conditions whereby the deformation is maintained constant. In the case of rotatory shearing, the force is applied as a couple C, and the deformation is measured by the angle of rotation α. The parameter to be determined is then $(\partial C/\partial T)_\alpha$ for different deformations.

Based on the preceding equations:

$$-\left(\frac{\partial C}{\partial T}\right)_\alpha = \left(\frac{\partial S}{\partial \alpha}\right)_T$$

and if the rubber has an ideal behavior, it is necessary that:

$$\left(\frac{\partial E}{\partial \alpha}\right)_T = 0$$

in which case:

$$\left(\frac{\partial A}{\partial \alpha}\right)_T = \left(\frac{\partial E}{\partial \alpha}\right)_T - T\left(\frac{\partial S}{\partial \alpha}\right)_T = \left(\frac{\partial C}{\partial T}\right)_\alpha$$

where A is the free energy. The first member is none other than the couple; the last member is in principle measurable directly. For several reasons, however, one of which is that experiments at very small deformations are difficult to carry out, some other procedure seemed preferable.

It can be shown that:

$$\left(\frac{\partial C}{\partial T}\right)_\alpha = -\left(\frac{\partial C}{\partial \alpha}\right)_T \cdot \left(\frac{\partial \alpha}{\partial T}\right)_C$$

The first factor in the second member is proportional to the shearing modulus; it is, therefore always positive. The second factor represents the change in deformation with temperature; it may be either positive or negative. Their product is equal to the derivative: $(\partial S/\partial \alpha)_T$.

The apparatus already described earlier in this paper was used in the experiments.

Each of the two factors was measured separately; it is important that each pair of values thus obtained refer to the same state of rubber and that this represents a reversible transformation. It is, therefore, indispensable to eliminate all effects such as plastic deformation or hysteresis. This condition is somewhat difficult to attain, for the relatively great thickness of the rubber prevents rapid heat exchange. A thermometer, the bulb of which had a diameter equal to that of the brass rod passing through the cylindrical rubber and placed in the same position, indicated that, when the temperature of the water was suddenly changed by 10 degrees, thermal equilibrium was not established until about the end of twenty minutes. About forty-five minutes at least had to be allowed to be certain that the torsion angle no longer varied, and each measurement of $\partial\alpha/\partial T$, which necessarily involved two determinations, required therefore at least one and one-half hours.

The influence of secondary effects was eliminated by the following method. This coefficient $(\partial\alpha/\partial T)_C$ was measured each 10 degrees from 20° to 70° C. First of all the rubber was held at 70° C under the smallest possible tension at which the effects were measurable until the torsion angle no longer varied appreciably during a period of two hours. The temperature was then raised to 75° C and held at this point for 45 minutes; then at 65° C for the same length of time, then at 75° C again, and so on. By recording each time the difference $\alpha_{75} - \alpha_{65} = \Delta\alpha_{70}$, a series of values was obtained which corresponded alternately to the rise and fall in temperature. The plastic deformation, which is additive in the first case and subtractive in the second case, tended to disappear in the mean of these values, $\overline{\Delta\alpha}_{10}$. This mean corresponds to a temperature 5° C higher and 5° C lower than the mean temperature of 70° C, so that $\Delta T = 10°$ C. Hence $(\overline{\Delta\alpha}/10)$ must approach the value $(\partial\alpha/\partial T)_C$ for the mean temperature of 70° C.

After this series of determinations had been made, the temperature of the water was changed to 60° C and held at this point until α did not vary in a period of two hours; from observations at 65° C and at 55° C it was then possible to calculate $(\partial\alpha/\partial T)_C$ at the mean temperature of 60° C. In this way all the $(\partial\alpha/\partial T)$ values were determined between 70° C and 20° C for a load of 45 grams. At a still lower temperature (15° C), the results were no longer valid, for the rubber became very sluggish.

During this first series of operations, the tension force was 45 grams, which corresponds to a couple of 1.55×10^5 dyne-cm. A second series of observations with a load of 95 grams made it possible to determine the corresponding

values of $(\partial\alpha/\partial T)_C$ for a couple of 3.26×10^5 dyne-cm.; a third series was carried out with a load of 145 grams, corresponding to a couple of 4.98×10^5 dyne-cm. The results of these measurements are shown in Table 2.

TABLE 2

VALUES OF $-(\partial\alpha/\partial T)_C$ IN DEGREES OF ANGLE PER DEGREE CENTIGRADE
(All values are to be multiplied by 10^{-3})

Force (grams)	20°	30°	40°	50°	60°	70°
45	—	2.2	2.3	2.2	1.9	1.8
95	4.5	4.2	4.2	4.2	4.2	3.9
145	7.8	8.0	6.4	6.1	5.6	5.5

To determine $(\partial C/\partial\alpha)_T$, each series of measurements was interrupted in the middle, the temperature was brought to the mean value for the particular series, and held until equilibrium was established; then the load was alternately increased and reduced by 5 grams. The $\Delta\alpha$ values thus obtained correspond to a change in the load of 10 grams, *i.e.*, to $\Delta C = 3.43 \times 10^4$ dyne-cm. The quotient $\Delta C/\Delta\alpha$ should be practically identical to the value of $(\partial C/\partial\alpha)_T$ for rubber when it is in the state where the corresponding $(\partial\alpha/\partial T)_C$ value has been measured. The results are shown in Table 3.

TABLE 3

VALUES OF $(\partial C/\partial\alpha)$ IN DYNE-CM. PER DEGREE OF ANGLE
(All values are to be multiplied by 10^3)

Force (grams)	20°	30°	40°	50°	60°	70°
45	265	250	243	250	246	254
95	268	250	254	245	242	253
145	274	250	253	251	255	257

It is somewhat difficult to estimate the experimental errors; they are certainly greater for $(\partial\alpha/\partial T)$ than for $(\partial C/\partial\alpha)$, and relatively greater for small couples. It is believed, however, that, in general, the precision is of the order of ± 10 per cent for $(\partial\alpha/\partial T)$ and about 2 per cent for $(\partial C/\partial\alpha)$.

One of the sources of error arises from possible slipping of the cylindrical rubber test-specimen on the axial rod or on the brass tube. There is no such slipping when the brass is thoroughly cleaned. By heating the apparatus with no tension for several days at 50–60° C, perfect adhesion between metal and rubber is obtained without compression and deformation of the latter and without the use of adhesives.

The rubber used in the tests was a commercial type (stopper), prepared from a mixture made up of rubber 100, sulfur 3, diphenylguanidine 1, aldol-α-naphthylamine 2, paraffin 3, and zinc oxide 5. This mixture was moulded and vulcanized in cylindrical form.

By multiplication of the corresponding values of Tables 2 and 3, division of the resulting values by the weight of rubber (13 grams), and multiplication by T, the values shown in Table 1 were obtained.

SHEARING AND ELONGATION

With the data in Table 3, it is possible to compare the deformations brought about by shearing with those resulting from stretching. These two types of

deformation are geometrically dissimilar, and only the accumulated energy can be compared.

According to Table 3, $\partial C/\partial\alpha$ is practically constant, at approximately 2.55×10^5. The free energy of the rubber subjected to couple C is then:

$$\int C \cdot d\alpha = \int C \frac{dc}{2.55 \times 10^5} \approx \frac{10^{-5}}{5.1} C^2 \text{ ergs}$$

Since the weight of the sample was 13 grams, the free energy per gram of rubber is:

$$A_C = \frac{10^{-5}}{5.1 \times 13} C^2 \text{ ergs} \tag{6}$$

The elongation corresponding to this free energy can then be calculated. For a cube 1 cm. on each side (weighing practically 1 gram), $A_l = \int f \cdot dl$.

It is known that the mean value of the stretch modulus is:

$$\epsilon = \frac{\partial f}{\partial l} \approx 0.4 \times 10^7$$

which is practically constant between 0 and 30 per cent elongation. If the elongation is expressed as Δl, then:

$$f = 1.4 \times 10^7 \Delta l$$

and

$$A_l = \int 1.4 \times 10^7 (\Delta l) dl = 0.7 \times 10^7 (\Delta l)^2 \tag{7}$$

If this energy is equal to that obtained by shearing, and in accordance with Equations (6) and (7):

$$(\Delta l)^2 = \frac{10^{-5}}{5.1 \times 13} \times \frac{10^{-7}}{0.7} C^2$$

where $\Delta l = 1.47 \times 10^{-7} C$.

Accordingly the three couples used in the experiments correspond to the following elongations:

Couple (dyne-cm.)	Elongation (percentage)
1.55×10^5	2.3
3.26×10^5	4.8
4.98×10^5	7.3

The couples which were chosen fall well within the range of elongations of 0 to 10 per cent, *i.e.*, within the range where the derivations from ideal behavior are particularly great.

RÉSUMÉ

The deviations of rubberlike materials from ideal behavior at low elongations or compressions arise from small changes in volume, which bring about considerable changes in internal energy and in entropy. On the contrary, when subjected to shearing, the behavior is ideal, even at very small deformations, for shearing does not bring about any change in volume.

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THE PROTECTION OF RUBBER AGAINST OXYGEN BY A DEACTIVATING EFFECT *

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It has already been shown by one of the authors[1] that certain substances protect vulcanized rubber against deterioration by oxidation and yet have practically no retarding effect on its rate of oxidation. The mechanism of the action of these agents is, therefore, different from that of antioxygenic agents, and it has been called a deactivating effect. The first substance which was found to manifest this hitherto unrecognized effect was mercaptobenzimidazole.

The attempt has been made to gain a better understanding of the conditions under which mercaptobenzimidazole is active, both alone and in the presence of an antioxygenic substance.

It was first found that mercaptobenzimidazole, in contrast to most antioxygenic agents, has no protective action against aging in the case of simple rubber sulfur vulcanizates, *i.e.*, vulcanizates which do not contain any other ingredients which are ordinarily added, notably accelerators, zinc oxide and plasticizers. Systematic experiments with these various types of ingredients show the indispensable part played by zinc oxide, in view of which it may be assumed that a zinc salt is formed during vulcanization by reaction of the zinc oxide with the acid group of the thiol. As a matter of fact, when zinc mercaptobenzimidazolate is added to a rubber-sulfur mixture, it protects the vulcanizate from aging. Furthermore, if the reaction of mercaptobenzimidazole with zinc oxide is rendered impossible by replacing the hydrogen of the SH group by a radical, there is no longer any protective effect. 2-Methylmercaptobenzimidazole, for example, shows no protective action under any conditions.

The deactivating effect is, however, not restricted or specific to zinc oxide; the mercaptobenzimidazoles of iron and magnesium, which were prepared in the present work, behave similarly[2]. The same is true of compounds belonging to related types, such as mercaptobenzoxazole and ethylene-bis(*N*,*N'*-phenylthiourea). On the other hand, further experiments[3] have shown that the combined use of an antioxygenic substance and a deactivating agent gives considerably increased protection against oxygen. In this case, there is a reciprocal reënforcement of the two effects, as may be seen by an examination of Figures 1 and 2. In the first place, measurements of the oxidizability (see Figure 1) show that mixture A + D reduces the rate of oxidation more than does the antioxygenic substance alone; in other words, there is a corresponding increase in antioxygenic effect. In addition, it will be seen that, for the same deterioration, *i.e.*, the same loss of tensile strength, the rubber containing A + D tolerated a higher percentage of oxygen than when only the deactivating agent alone was present. This points to an increase in the deactivating effect.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Comptes Rendus de l'Académie des Sciences*, Vol. 223, No. 19, pages 724–726, November 4, 1946.

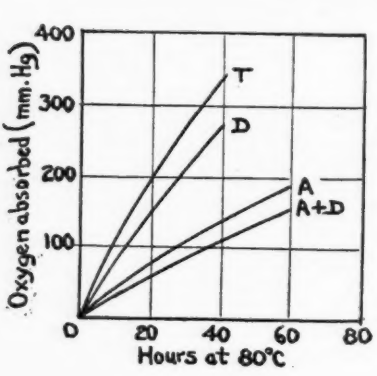

FIG. a

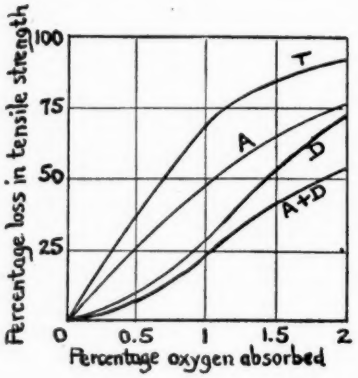

FIG. b

T = control mixture
A = T + 2 parts of antioxygenic agent
D = T + 2 parts of deactivating agent
A + D = T + 1 part of antioxygenic agent + 1 part of deactivating agent
Antioxygenic agent = phenyl-β-naphthylamine
Deactivating agent = mercaptobenzimidazole

Furthermore, in the case of two antioxygenic substances, A and A′, of the same character, it has been found that a mixture of A and A′ has, when the combined amount is the same as the amount of one of the individual substances, a greater antioxygenic power than that of either of the two substances alone. This is true also of a mixture of two similar deactivating agents D and D′, which has a disproportionately great deactivating power compared to that of either agent alone. It had previously been found that, from a practical point of view, every protective substance combines these two mechanisms, with one or the other of the mechanisms predominating. In view of this, the results shown in Figures 1 and 2 can be explained logically, *viz.*, the combined use of the two types of protective agents really amounts to the use of two antioxygenic substances and two deactivating substances.

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THE INTERACTION BETWEEN RUBBER AND LIQUIDS. VIII. A NEW EXAMINATION OF THE THERMODYNAMIC PROPERTIES OF THE SYSTEM RUBBER + BENZENE *

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Huggins has shown[1] that the Gibbs' free energy of dilution, ΔG_0, of a rubber solution can in general be expressed as a function of the volume fraction of rubber, v_r by an equation of the form:

$$\Delta G_0 = RT\{\ln (1 - v_r) + v_r + \mu v_r^2\} \qquad (1)$$

where μ is a constant, and the term μRTv_r^2 is closely related to the heat of dilution ΔH_0. In the previous paper of this series[2], ΔH_0 was estimated for natural rubber in a range of liquids by calorimetric measurements of the heats of mixing of these liquids with dihydromyrcene. In general, it was found that, for dihydromyrcene, $\Delta H_0/v_r^2$ was nearly constant, suggesting the same to be probably true for rubber. This conclusion is not in agreement with the data reported earlier for rubber + benzene[3], according to which $\Delta H_0/v_r^2$ increases as v_r increases. The accuracy attained in this earlier investigation was not, however, sufficient for any great reliance to be placed on values of ΔH_0, since these were based on rather small temperature coefficients of the measured $\Delta G_0/T$. In this paper, the problem of the constancy of $\Delta H_0/v_r^2$ is reconsidered on the basis of new experimental work along two lines: (1) a direct measurement of the heat of solution of a low molecular polyisoprene; (2) more refined vapor pressure measurements, giving more reproducible temperature coefficients. Of the four concentration ranges previously studied, only the two intermediate ones have been reinvestigated, since these were considered to give the least reliable heats of dilution.

THE HEAT OF SOLUTION OF POLYISOPRENE IN BENZENE

A sample of a polyisoprene of molecular weight[4] about 4,000 was prepared by J. L. Bolland by the sodium-catalyzed polymerization of isoprene in the presence of toluene[5]. The heat of solution in benzene at 16° C was measured by (Miss) J. Ferry, employing the method previously described[2]. A 50 per cent solution of polyisoprene in light petroleum was introduced into the outer bulb (Figure 1[2]) through a side tube, which was subsequently sealed off, the naphtha being removed by cautious evacuation to avoid splashing. The amount of polyisoprene introduced was estimated by weighing. Successive additions of benzene were then made as previously described, but it was necessary to allow time (about half an hour) for complete dissolution of the polymer, so the correction for heat losses was larger than in the earlier work. The results of two series

* Reprinted from the *Transactions of the Faraday Society*, Vol. 42, Nos. 6–7, pages 507–517, June–July 1946.

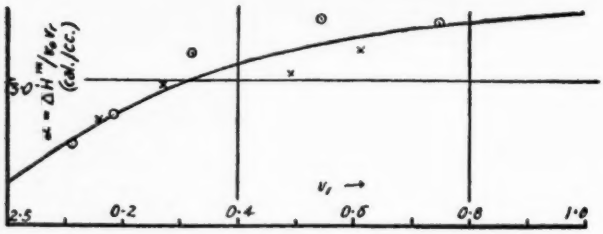

FIG. 1.—Heat of mixing of polyisoprene and benzene.

of measurements are shown in Figure 1, in which the constant α is plotted as a function of the volume fraction v_r of the polymer. α is defined, as before, as:

$$\alpha = \Delta H^m/v_r(1 - v_r) \tag{2}$$

where ΔH^m is the heat absorbed when v_r cc. of polymer is dissolved in $(1 - v_r)$ cc. of benzene. Although the experimental accuracy becomes less as the polymer is progressively diluted (decreasing v_r), there appears to be a very definite trend in α, as shown by the smooth curve drawn in. The heat of dilution ΔH_0 can be calculated from this curve by means of the equation[2]:

$$\Delta H_0 = V_0 v_r^2 \left\{ \alpha - (1 - v_r) \frac{\partial \alpha}{\partial v_r} \right\} \tag{3}$$

where V_0 is the molar volume of benzene. The result is shown in Figure 2, where $\Delta H_0/v_r^2$ is plotted against v_r, and is seen to be very dependent on v_r. No evidence of such behavior was found in the mixing of squalene and dihydromyrcene with benzene[2], where α was constant within experimental error. The squalene data do not entirely rule out the possibility of a small trend in α, as is seen by the detailed results set out in Table I.

The last column gives α values read from a smooth curve assumed to be of the same shape as the polyisoprene curve. The only point deviating significantly from experiment is the last one, which must be considered the least accurate owing to the rather small squalene concentration. The squalene curve of Figure 2 is $\Delta H_0/v_r^2$ calculated from the α values of the last column of Table I,

TABLE I

HEAT OF MIXING OF SQUALENE AND BENZENE

	α(cal. per cc.)	
v_r	Exptl.	Smoothed
0.871	4.01	4.03
0.716	4.04	4.01
0.607	3.99	4.00
0.527	3.97	3.98
0.451	3.99	3.96
0.364	3.92	3.93
0.244	3.91	3.89
0.067	3.94	3.81

and must be taken to give an upper limit to the dependence of $\Delta H_0/v_r^2$ on v_r. There is no experimental evidence that α depends in this way on v_r for dihydromyrcene + benzene, so that $\Delta H_0/v_r^2$ is constant (Figure 2).

The value of $\Delta H_0/v_r^2$ found for polyisoprene increases from about 100 at $v_r = 0$ to 287 cal. per mol. at $v_r = 1$. The latter is somewhat less than the

figure (310) estimated for rubber by extrapolation from the dihydromyrcene value[2]. The two figures are not quite strictly comparable, for two reasons: (1) the polyisoprene was prepared by sodium-catalyzed polymerization, and there is evidence[6] that this reaction leads to a considerable proportion of 1:2 addition. (2) Toluene was used to control the molecular weight of polymer produced, and a spectroscopic investigation, for which we are indebted to H. P. Koch, suggests that one molecule of toluene is incorporated in each molecule of polymer.

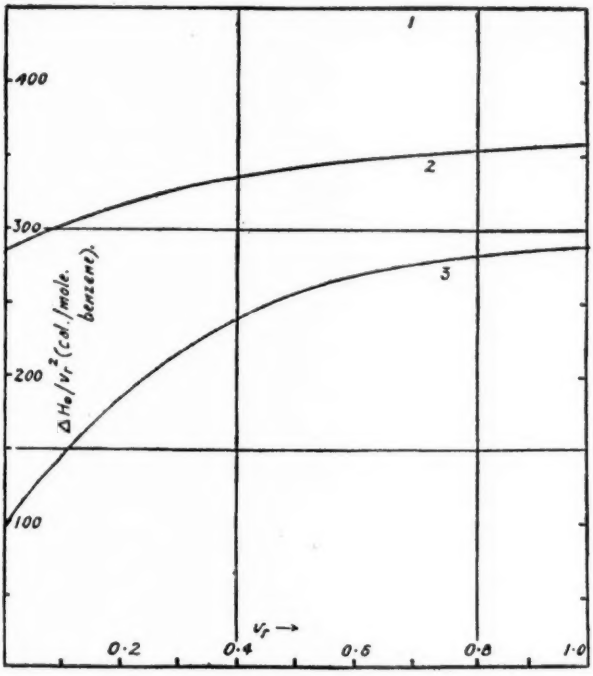

FIG. 2.—Heats of dilution by benzene from calorimetric data. (1, Dihydromyrcene; 2, Squalene; 3, Polyisoprene.)

NEW VAPOR PRESSURE MEASUREMENTS ON THE RUBBER–BENZENE SYSTEM

Over an intermediate concentration range, a convenient method of obtaining relative vapor pressure data for a binary system such as rubber + benzene, where one of the components is involatile, is to balance the vapor pressure of the solution kept at constant temperature, T_1, say, in a communicating system against the vapor pressure of the pure solvent kept at a lower temperature, T_2. In a given series of experiments, for example, with $T_1 = 35°$ C, the concentration range between $v_r = 0.35$ and 0.86 was covered with values of $\Delta T = T_1 - T_2$ lying between 0.74 and 18 degrees. Measurements were carried out in a thermostat divided by a fixed partition into two parts, which were independently controlled at the definite fixed temperatures, T_1 and T_2. The partition contained a sliding gate which carried the vapor pressure apparatus.

In a first series of experiments the apparatus shown diagrammatically in Figure 3*a* was employed, consisting simply (on the hot side of the double thermostat) of a bulb A, containing a weighed amount of rubber, communicating directly through the gate C with a calibrated tube B (on the cold side), in which the volume of benzene, when equilibrium was reached, could be read off by direct observation. Hence, knowing the dimensions of the apparatus and the total volume of benzene in the system, the weight of benzene in the rubber phase was determined. The vapor pressure of the solution at T_1, kept constant at 35.01° ± 0.02° C, is equal to that of the solvent at T_2, which has, in this method, to be obtained from a vapor pressure curve determined independently. In calculating the $\Delta G_0/Tv_r^2$ data[7] (see Figure 4) Scatchard's vapor pressure data[8] were employed.

The benzene used in the above experiments, which was from the same stock as that employed in the isopiestic and calorimetric experiments, was A.R. reagent, which had been carefully fractionated and dried over sodium. Before sealing off the apparatus *in vacuo*, the benzene sample was again dried over a

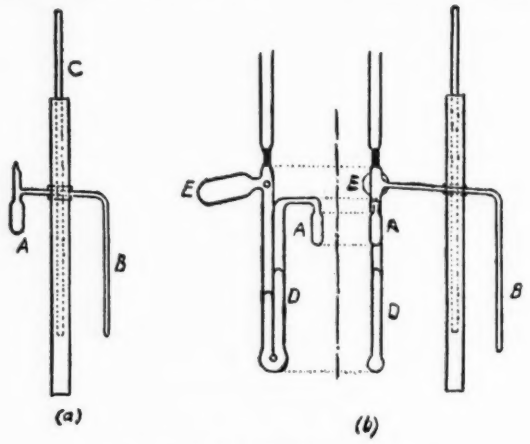

FIG. 3.—Vapor pressure apparatus.

molten sodium surface and outgassed. The vapor pressure of this stock benzene, determined by a direct manometric method, was, however, about 3 mm. higher at 25° C than the most reliable reference data, while its melting point was 0.74° C too low. For the subsequent vapor pressure experiments a sample of A.R. benzene was freed from impurities by fractional crystallization repeated until a constant melting point of 5.56° C (in presence of P_2O_5) was obtained. This value compares very favorably with Scatchard's value[8], namely, 5.53° C (in presence of $CaCl_2$) and Le Blanc and Möbius' value[9] 5.55° C. The measured vapor pressure at 25° C, namely, 95.3_2 ± 0.05 mm. Hg. (0° C), for this sample, is still, however, 0.9 mm. higher than that recorded in the I.C.T.

The experiments with this purified sample of benzene were carried out in a modified form of the first apparatus, Figure 3*b*, in which a mercury manometer D of about 20 cm. range was introduced between A and B on the hot side of the double thermostat. This arrangement, although not so simple to handle, had two advantages over the first, namely: (1) that a somewhat greater range

of concentrations could be covered for a given conveniently accessible experimental range of ΔT values and (2) that, by freezing out all the benzene at B, the mercury from D meantime being run into the bulb E, the vapor pressure of the pure benzene itself could be checked in each experiment. The experimental results are plotted in Figure 4.

All the free energy data have been corrected for gas imperfection. The possible observational error in determining $\Delta G_0/Tv_r^2$ in these experiments varied from 6 per cent for $v_r = 0.35$ to 2 per cent for $v_r = 0.8$, while the possible error in determining v_r itself varied between 0.3 and 0.5 per cent over the same range. From Figure 4 it will be seen that the data for the different types of measurement and apparatus check together within the experimental error and that there is no discernible systematic deviation in the $\Delta G_0/Tv_r^2$ data obtained using the stock benzene from that using the purified sample.

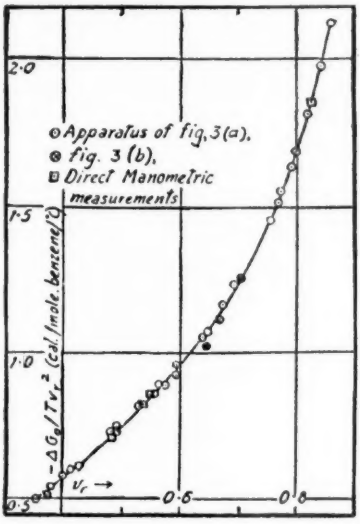

FIG. 4.—Gibbs' free energy of dilution of rubber by benzene from vapor pressure data at 35° C.

In all experiments the samples of highly purified intermediate molecular weight rubber were thoroughly out-gassed at 70° C before sealing off *in vacuo*.

To obtain the heat of dilution of rubber by benzene, temperature coefficients were measured at a few convenient concentrations. The data obtained, which are clearly subject to considerable experimental uncertainty, are shown in Figure 5. The values of $\Delta H_0/v_r^2$ obtained from the slopes of these $\Delta G_0/Tv_r^2$ versus $1/T$ curves will be considered below.

FREE ENERGY OF DILUTION OF OLIVE OIL BY BENZENE

A determination of the thermodynamic data on the olive oil + benzene system has been made for use in conjunction with the isopiestic measurements (see below). For higher weight fractions of olive oil, direct manometric vapor pressure measurements at 25° C have been employed, while for lower weight fractions freezing point depression measurements have been used. The re-

ciprocals of the apparent molecular weight (M^1), calculated from the observed vapor pressures, using the formula:

$$\frac{1}{M^1} = \frac{1}{78.11} \cdot \frac{p_0 - p_m}{p_m} \cdot \frac{W_0}{W_s} \tag{4}$$

are plotted in Figure 6. W_0 and W_s are the weight fractions of benzene and oil.

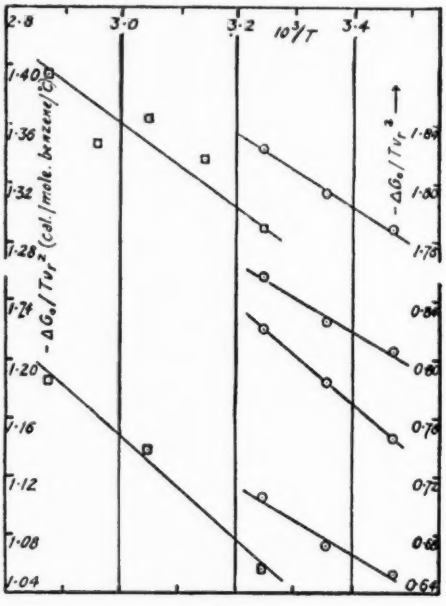

FIG. 5.—Temperature coefficient of Gibbs' free energy of dilution (vapor pressure data).

The freezing point experiments were carried out with a simple Beckmann type cryostat, care being taken, however, to prevent as far as possible the condensation of moisture in the solution during the course of the measurements by the continuous passage of a slow stream of dry air saturated with benzene vapor. In this case $1/M^1$ is calculated from the observed depressions Δ by the relation:

$$\frac{1}{M^1} = \frac{\Delta}{5120} \cdot \frac{W_0}{W_s} \tag{5}$$

From the cryoscopic data referring to a temperature of 5.56° the points plotted in Figure 6 were calculated, using the ΔH_0^s data determined calorimetrically (see below) for this system.

From Figure 6 extrapolated molecular weight of olive oil at infinite dilution is 830, which is considerably lower than the theoretical value for pure triolein, namely, 885. It should be pointed out also that the above data do not agree at all well with the earlier measurements of Gee and Treloar[3]. The present data are considered to be more precise.

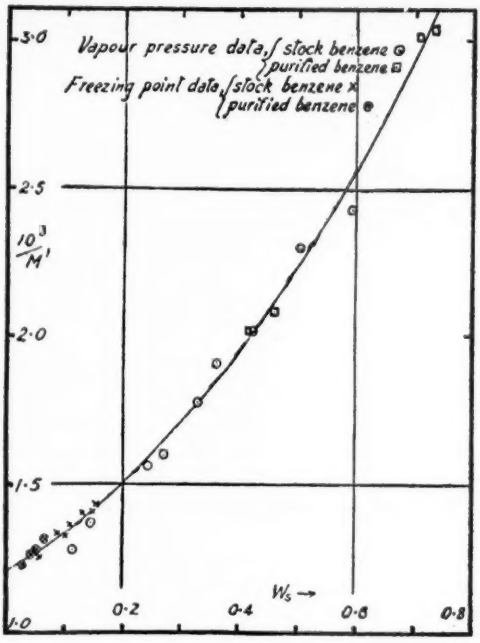

FIG. 6.—Apparent molecular weight of olive oil in benzene at 25° C.

THE HEAT OF MIXING OF OLIVE OIL AND BENZENE

The heat of mixing of olive oil and benzene at 16° C was determined calorimetrically by (Miss) J. Ferry, employing the method previously described. The results are given in Table II, in the form of the "constant" α. Within

TABLE II

HEAT OF MIXING OF OLIVE OIL AND BENZENE

v_0	α(cal. per cc.)
0.233	2.75
0.477	2.88
0.680	2.91

the accuracy needed for our present purpose, α is substantially constant, so the heat of dilution ΔH_0^s of olive oil by benzene is given by $\Delta H_0^s = \alpha V_0 v_r^2 = 250\ v_r^2$ cal. per mol. benzene, where v_r is the volume fraction of olive oil.

DETERMINATION OF THE ISOPIESTIC RATIO BETWEEN RUBBER AND OLIVE OIL

To improve the precision with which isopiestic ratios could be measured, the still shown in Figure 7 was designed. Compared with the previous type[3], it permits more rapid distillation and improved temperature equalization between the two solutions. Finely cut rubber was weighed into the inner tube A through the large hole blown in its side. Olive oil was weighed through E into the bulb B, and benzene pipetted in, the relative amounts being chosen

so that at equilibrium the benzene was approximately evenly distributed between rubber and oil. After evacuation and outgassing, the still was sealed off at C. The amount of benzene then present in the still was determined by comparing its weight, together with that of the joint removed, with the weight

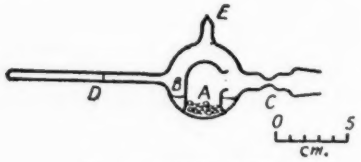

FIG. 7.—Isothermal still.

of the empty apparatus, a suitable buoyancy correction being applied. The still was then mounted horizontally in a thermostat controlled to ±0.01° C, and left 24 hours or more to attain equilibrium. At intervals the still was turned so that the calibrated tube D was vertical, half an hour allowed for the oil solution to drain, and its height in D measured with a cathetometer. When equilibrium had been attained, the still was transferred to another thermostat and a further measurement made.

The volume of oil solution measured in this way requires correction for the small amount which sticks to the bulb. This was determined by carrying out a blank experiment in which the rubber was omitted and comparing the volume of oil solution draining into the side tube with that known to be in the still, allowance being made for the benzene vapor. Applying this drainage correc-

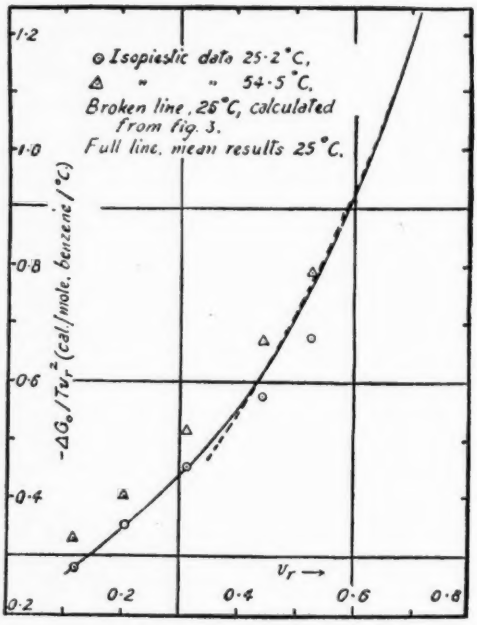

FIG. 8.—Gibbs' free energy of dilution of rubber by benzene.

tion to the equilibration experiment, the amount of benzene on the rubber was obtained. Typical results are given in Table III.

TABLE III

DISTRIBUTION OF BENZENE IN EQUILIBRATION EXPERIMENT

	25.2° C	54.5° C
Vol. of oil solution measured (cc.)	1.796	1.752
Add drainage correction	.015	0.012
Total volume of oil solution	1.811	1.764
Weight of benzene on oil	1.327	1.234
Weight of benzene in vapor (calculated)	0.047	0.152
Weight of benzene on rubber (by difference)	1.142	1.130
Total weight of benzene introduced	2.516	2.516

A series of measurements of this kind gave the following pairs of isopiestic solutions, W_s and W_r being the weight fraction of oil and rubber.

These data, together with those reported above for the free energies of the oil solutions, enable the free energy and heat of dilution of rubber solutions to be calculated. The free energies are plotted in Figure 8, in the form of $\Delta G_0/Tv_r^2$. The 25° C points do not agree very well with the curve (shown dotted) calculated from Figure 4 by means of the heats of dilution reported below. The discrepancy is larger than was expected, and suggests a small systematic error in one or both sets of data. In this connection, two points have to be borne in mind. (1) The region $v_r = 0.4$ to 0.5 is near the limit of both methods of investigation and experimental errors are probably at their maximum. (2) The method of plotting results in an amplification of any experimental error in determining concentrations by a factor of as much as 5 in this concentration region. Thus if v_s is 1 per cent too low, v_r will be about 1 per cent too high, $-\Delta G_0$ about 2 per cent too low, so a point on this plot will be about 5 per cent too low. The full line of Figure 8 has been taken as the best representation of the Gibbs' free energy of dilution at 25° C for v_r between 0.1 and 0.7.

THE HEAT AND ENTROPY OF DILUTION

Figure 9 gives the heats of dilution calculated from the individual isopiestic experiments, and from the direct vapor pressure data (Figure 5), together with the values found previously[3] for very high and very low rubber concentrations. The experimental accuracy is clearly not sufficient to determine the precise shape of the curve, but it appears to be established beyond reasonable doubt that $\Delta H_0/v_r^2$ decreases progressively with increasing dilution. The curve actually drawn in is based on the shape of the polyisoprene curve, and is taken to the limiting value of $\Delta H_0/v_r^2 = 310$ cal. per mol. at $v_r = 1$.

TABLE IV

COMPOSITIONS OF ISOPIESTIC SOLUTIONS

25.2° C		54.5° C	
W_s	W_r	W_s	W_r
0.0208_3	0.121_9	0.0225_7	0.120_5
0.0693	0.208_9	0.0741	0.208_7
0.167_3	0.318_0	0.176_2	0.320_0
0.303_5	0.447_3	0.319_7	0.451_9
0.394_0	0.530_7	0.413_1	0.536_1

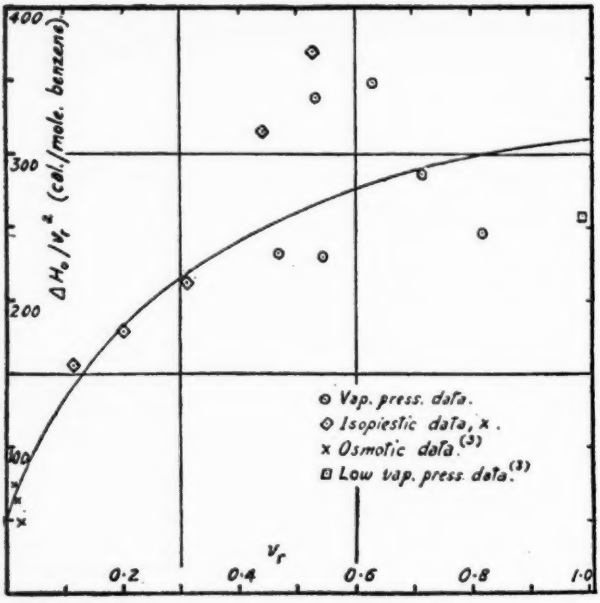

FIG. 9.—Heat of dilution of rubber by benzene.
(⊙ Vapor pressure data. ◇ Isopiestic data. × Osmotic data.[3]
⊡ Low vapor pressure data.[3])

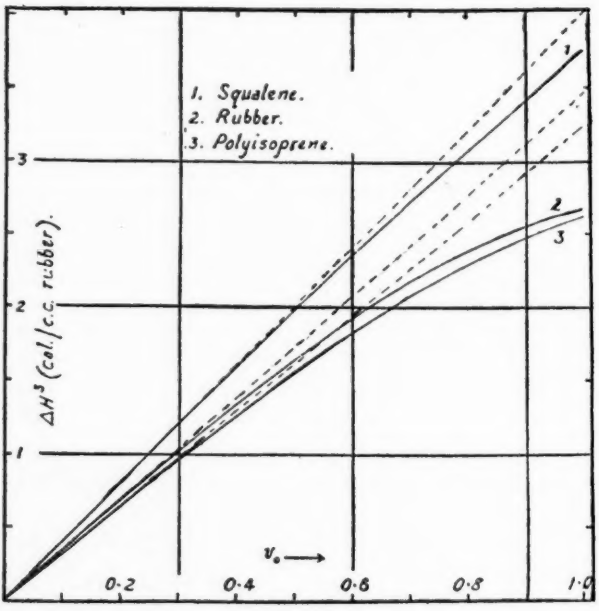

FIG. 10.—Heats of solution in benzene.

The data for squalene, polyisoprene, and rubber are compared in Figure 10 by plotting the heat of solution ΔH^s, *i.e.*, the heat absorbed when 1 cc. of rubber absorbs $v_0/1 - v_0$ cc. of benzene. This is given by:

$$\Delta H^s = \alpha v_0 = \frac{1}{V_0}\int_0^{v_0} \frac{\Delta H_0}{v_r^2}\, dv_0 \qquad (6)$$

The total heats of solution (*i.e.*, when $v_0 \to 1$) are: squalene 3.7_8 cal. per cc., polyisoprene 2.6_4 cal. per cc., rubber 2.6_9 cal. per cc.

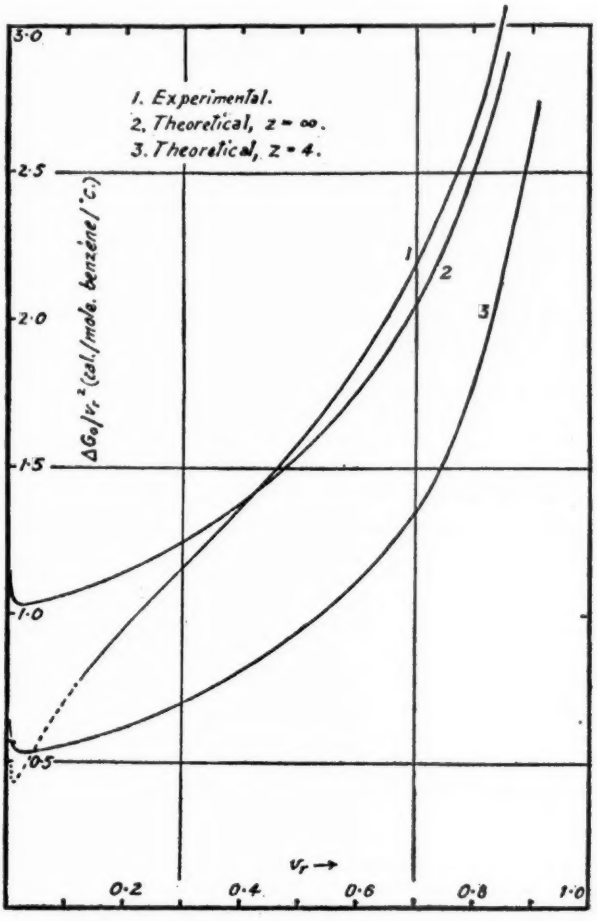

FIG. 11.—Entropy of dilution of rubber by benzene.

Figure 11 shows the entropy of dilution obtained from the smoothed free energy curve of Figure 8, and heat of dilution (Figure 9). The dotted extension was deduced by extrapolating Figure 8 to meet the osmotic data previously reported[3]. For comparison curves are given calculated from Miller's theoretical

equation[10]:

$$\Delta S_0 = -R\left[\ln(1-v_r) - \frac{Z}{2}\ln\left\{1 - \frac{2v_r}{Z}\left(1 - \frac{1}{x}\right)\right\}\right] \qquad (7)$$

where Z is the coördination number and x the ratio of the molar volumes of rubber and liquid. The two curves are for $Z = \infty$, $Z = 4$, with $x = 5000$, and there is evidently a very considerable discrepancy between the shapes of theoretical and experimental curves. The former should strictly be corrected for the effect of a finite heat of mixing, but detailed analysis[11] shows this to be small. Taking $\Delta H_0/v_r^2 = 310$ cal. per mol. throughout, the calculated value of $\Delta S_0/v_r^2$ for $Z = 4$ is reduced for $v_r > 0.5$ (approx.) and increased for $v_r < 0.5$, but the maximum correction is less than 0.04 cal. per mol. ° C and is, therefore, almost negligible. This departure of the entropy of dilution from the theoretical form must of course balance the fall of $\Delta H_0/v_r^2$ for small v_r, since it has already been shown that the free energy of dilution has almost the theoretical form.

DISCUSSION

The high value of the entropy of dilution over most of the concentration range has already been noted[2]. The excess over the theoretical expectation is of the same order as that found in benzene-cyclohexane mixtures[8] and may well arise from a breakdown in the ordered structure of liquid benzene on its absorption by rubber. The new feature brought out in this work is the rapid fall in both $\Delta H_0/v_r^2$ and $\Delta S_0/v_r^2$ with increasing dilution. Comparison with dihydromyrcene, squalene and polyisoprene suggests strongly that the phenomenon is due essentially to the long-chain character of the rubber. At least two factors might contribute to the low ΔH_0 value at low rubber contents: (1) A change in the form of the rubber-benzene contacts, arising, *e.g.*, from the anisotropy of the benzene molecule. It seems highly improbable that this would be specific to long chains, and this possibility is therefore neglected. (2) The number of rubber-rubber contacts might be greater in dilute solution than assumed in the present theory. This effect could arise in two possible ways: (1) from intramolecular contacts resulting from the coiling back on itself of a single molecule, an effect which is a normal statistical expectation at infinite dilution, and (2) from a possible dependence of ΔH_0 on the effective surface area of rubber rather than on its volume fraction[12]. The effect of the second of these possibilities, which can be calculated explicitly using the formulas of Orr[11], however, does not seem likely to be important since it requires the lowering of $\Delta H_0/v_r^2$ to occur mainly for large values of v_r and to be almost as great for squalene as for rubber. The thermal data therefore lead to the conclusion that a significant degree of coiling of individual rubber molecules, leading to intramolecular contacts, occurs in dilute solutions. This view finds qualitative support in the fall in the entropy of dilution occurring parallel with that in ΔH_0. An estimate of the degree of coiling can be made from the total heats of solution reported here, by assuming that the heat of mixing, per rubber-benzene contact, is independent of concentration. It is clear that if the rubber molecule eventually became completely surrounded by benzene, the total heat of solution would be equal to α_1, the value of α at $v_r = 1$. Hence the fraction of rubber segments in contact with benzene in an infinitely dilute solution is given by the ratio of the total heat of solution to α_1. The experimental values of this ratio are: squalene $\leqslant 0.94$, polyisoprene 0.81, rubber 0.77. The

form of the heat of solution curves (Figure 8) suggests that this effect of coiling in introducing additional rubber-rubber contacts begins to be significant at quite high rubber contents, as indicated by the departure of the curves from the broken straight lines.

It is important to note that this interpretation of the rubber-benzene data solutions in general $\Delta H_0/v_r^2$ should fall progressively with increasing dilution, with a corresponding fall in $\Delta S_0/v_r^2$, the magnitude of the effect depending, to some extent, on the heat of mixing. No other data of sufficient extent and accuracy are yet available to test this conclusion.[13].

SUMMARY

New vapor pressure data are reported for rubber-benzene mixtures, and used to calculate thermodynamic functions for the system. The heat of dilution is comparable with that measured calorimetrically for a polyisoprene of low molecular weight. Comparing the results with the available theoretical calculations it is shown that a significant contribution to the entropy and heat of dilution of polymer solutions at low concentrations results from the occurrence of polymer-polymer contacts within individual molecules due to statistical kinking.

Our thanks are due to J. L. Bolland, (Miss) J. Ferry, and H. P. Koch for the experimental assistance acknowledged in the text.

The work described in this paper forms part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

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[12] Gee and Treloar, *Trans. Faraday Soc.* **38**, 147 (1942); Gee, *Trans. Faraday Soc.* **38**, 418 (1942); Orr, *Trans. Faraday Soc.* **40**, 320 (1944).
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THE INTERACTION BETWEEN RUBBER AND LIQUIDS. IX. THE ELASTIC BEHAVIOR OF DRY AND SWOLLEN RUBBERS *

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Earlier papers of this series[1] have been concerned with the equilibrium properties of rubber solution and gels free from mechanical restraint. A closely related topic is that of the effects of liquids on the elastic behavior of vulcanized rubbers. Flory[2] has given a statistical thermodynamic treatment of this problem, but the experimental results recorded below appear to be the only ones available up to the present. It will be shown that they differ very significantly from the theoretical predictions, and also throw some light on the deviations of the elastic behavior of dry rubbers from that to be anticipated from the statistical analyses of Wall and others[3]. In attempting to trace the origin of these discrepancies, the problem of the temperature coefficient of elasticity has been reëxamined and new experimental methods and results are given below. The first section of this paper records the new data, and is followed by discussions of the thermodynamics and mechanism of elastic extension.

TENSION MEASUREMENT

A strip of rubber about 5 mm. wide × 0.8 mm. thick was gripped in a pair of clamps, of which the lower was fixed, while the upper was suspended from either a simple spring balance or one arm of a beam balance. The lower clamp carried a tube surrounding the strip, with a ground cap having a capillary extension through which the suspension wire passed. Swollen rubbers could then be extended without appreciable loss of liquid by evaporation. The central portion of the strip was marked by inserting two fine tungsten wires, 3 cm. apart, perpendicular to the broad face of the strip. The shielding tube was immersed in a clear cylindrical Dewar vessel, through which water from a thermostat was circulated. Stress strain curves up to moderate extensions were measured with the strip first dry, and then swollen, the strip being left overnight after partial swelling to allow the liquid to distribute itself evenly. The degree of swelling was calculated from the unstrained length, swelling being assumed isotropic. The dry rubber showed slight hysteresis effects, although ten minutes were allowed for each point; all the swollen rubbers were substantially free from this trouble.

Figure 1 gives some typical curves obtained with a pure-gum natural rubber compound (A, appendix) swollen in toluene. The results are given in the form of the function, $\chi = \dfrac{f}{TA_0(l/l_0 - l_0^2/l^2 v_r)}$, where f is the tension in a strip of swollen rubber of length l, volume fraction of rubber v_r at temperature T; l_0 and

* Reprinted from the *Transactions of the Faraday Society*, Vol. 42, Nos. 8–9, pages 585–598, August-September 1946. The author takes the opportunity offered by this reprinting to revise the ordinate scales of Figures 6 and 7(a), which were incorrect in the original version.

A_0 are the length and cross-section of the dry unstrained strip, also at T. It is evident that χ, which, according to Flory's statistical theory (see below), should be a constant, depends both on the extension and on the degree of swelling. Figure 1 suggests strongly that χ tends to become more nearly constant as the rubber is progressively swollen, and becomes substantially constant for small extensions at sufficiently high degrees of swelling. Similar behavior is shown by other rubbers which have been examined. Results for four synthetic

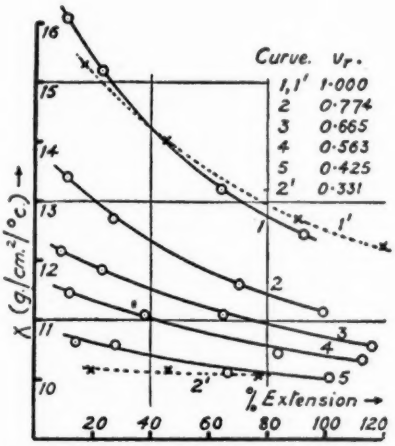

FIG. 1.—Dependence of an extension and swelling (natural rubber in toluene).

rubbers (B-E, appendix) are given in Figure 2. The values of χ in Figures 1 and 2 are not strictly equilibrium values (see discussion below), but errors arising from this fact have been shown to be insufficient to affect materially the form of the curves. It is of special interest to discover whether the limiting value of χ for highly swollen rubbers is independent of the swelling agent. Experiments designed to test this were carried out in a different way, thicker strips of rubber (about 4 mm.) being employed, and the tensions measured with the strip immersed and fully swollen in the liquid (1 to 2 days swelling of the stretched strip was allowed before measuring the strain). The swelling was then not the same as that of the unstretched strip, and was therefore determined, after the tension had been measured, by cutting out the marked central portion, surface drying and weighing. The dry weight was obtained by subsequent evaporation of the liquid. Only a single point could be determined from each experiment, and uncertainties are therefore introduced into the comparison by variations between nominally similar strips of rubber. Nevertheless the results (Figure 3) show that over a wide range of swelling, χ tends to a limiting value which is at least approximately the same for a range of liquids.

THE TEMPERATURE COEFFICIENT OF TENSION

Several previous attempts have been made to measure the temperature coefficient of the tension, but the problem is a rather difficult one, and the results cannot be considered completely satisfactory[4]. The main difficulty lies in ensuring that the measurements made represent true equilibrium states of the rubber. Anthony, Caston and Guth[5] have reported data for an 8 per cent

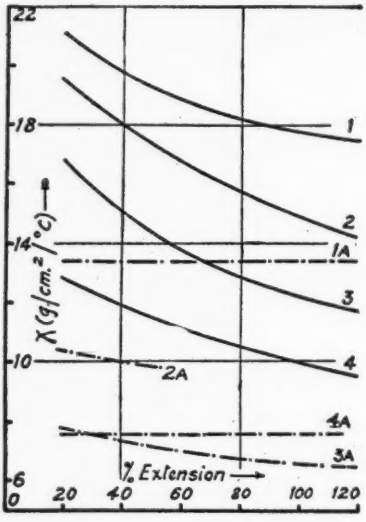

FIG. 2.—Effect of benzene on elastic modulus of synthetic rubbers at 25° C.

1. Buna-N, dry
1A. Buna-N, $v_r = 0.483$
2. Thiokol-FA, dry
2A. Thiokol-FA, $v_r = 0.520$
3. Neoprene-GN, dry
3A. Neoprene-GN, $v_r = 0.347$
4. GR-S, dry
4A. GR-S, $v_r = 0.376$

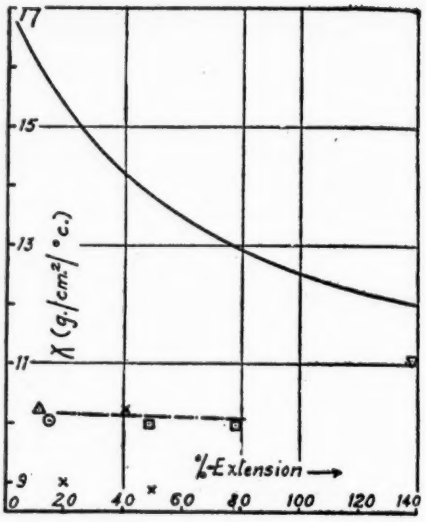

FIG. 3.—Effect of liquids on elastic modulus of natural rubber A at 25° C.

⊙ Benzene $v_r = 0.17$
△ Chloroform $v_r = 0.14$
× Petroleum ether $v_r = 0.27$
⊡ Kerosene $v_r = 0.317$
▽ Methylethyl ketone $v_r = 0.52$
Full line, $v_r = 1$
Broken line, toluene $v_r = 0.313$ from Figure 1.

sulfur vulcanizate of natural rubber, obtained as follows. A strip of rubber was extended and maintained at the highest temperature at which measurements were to be made. The tension was then observed to fall with time, rapidly at first, and then more and more slowly. When the rate became "small", the tension was recorded, and the temperature then lowered in steps, keeping the length constant[6], the tension being noted at each temperature. The temperature was then raised again in similar steps and tension again measured. The cycle of temperature variation was carried through quite rapidly (about 45 minutes) for a total change of $\pm 60°$ C, involving some dozen tension measurements, and under these conditions was found to be reversible. A similar experimental technique was employed by Roth and Wood[7] in studies of pure-gum accelerated compounds of GR-S and of natural rubber, except that in most cases the extension ratio rather than the length was maintained constant during the cycle of temperature change.

A disturbing feature of this experimental technique is the very limited degree of reversibility attained. If the initial relaxation was carried out at 50° C (say) the temperature could be lowered and then returned to 50° C reversibly, but if it was raised say to 60° C, further relaxation occurred. A new "reversible" stress-temperature curve could then be measured provided a temperature of 60° C was not exceeded. While the thermodynamic data obtained were not very dependent on the relaxation temperature actually employed, the position is clearly unsatisfactory. In an attempt to resolve this difficulty,

several alternative experimental techniques have been examined. To exclude as far as possible irreversible changes due to oxidative degradation, most of the work was done *in vacuo*. A strip of a pure-gum natural rubber compound (A) was provided with two reference wires, gripped in a pair of clamps, and loaded by a dead weight. The upper clamp was then suspended from a hook in a glass tube which could be evacuated and sealed. A side tube contained a little 40/60 petroleum ether, which could be distilled on to the rubber when desired and withdrawn again by cooling the side tube in liquid oxygen. Keeping the rubber dry the variation of length with temperature was investigated, behavior similar to that reported by Anthony, Caston and Guth[5] being observed. Use was then made of the petroleum ether to facilitate attainment of equilibrium at a given temperature, and very different results were observed. Some typical measurements are recorded in Figure 4, which represents the result of a series of observations on a single strip, maintained under constant load throughout, the extensions being of the order of 40 per cent. The strip was first allowed about twenty

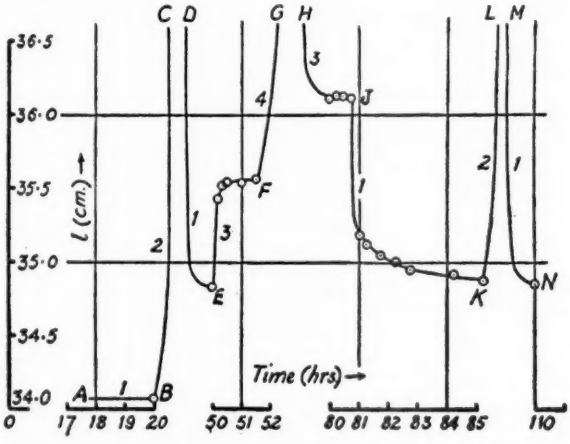

FIG. 4.—Temperature coefficient of length at constant load (1, rubber dry, 25.4° C; 2, swollen, 25.4° C; 3, dry, 0° C; 4, swollen, 0° C).

hours to reach an apparently constant length at 25° C (A-B), then maintained at 25° C while petroleum was distilled on (B-C) and removed again (D-E). The length (E) was then much greater than the previous apparent equilibrium value (B). Keeping the rubber dry, the temperature was lowered to 0° C, the length increasing and speedily becoming constant (E-F). Successive swelling (F-G) and drying (H-J) at 0° C, gave however a much greater length (J instead of F). Raising the temperature to 25° C, with the rubber dry, now produced a contraction, rapid at first, but continuing slowly for several hours (J-K) towards a value very close to the previous 25° value (E). Swelling (K-L) and drying (M-N) at 25° C again brought the length to the same value (N). In further experiments of this kind it was found that, provided the rubber was allowed to swell at each temperature, reversible temperature coefficients could be obtained even though the lower temperature was measured first.

These results show that length-temperature data can be obtained which are independent of the previous thermal history of the sample; they do not of course prove that such values are true equilibrium values, since the equilibrium

is always approached in the same way. During the process of drying out the solvent, the rubber is contracting and the lengths found might be systematically too great. Since any such effect would clearly be greatest at low temperatures, the temperature coefficients measured might be too large. Evidence has been found that this does actually occur to a small extent for temperatures below 20° C, especially at extensions of less than 20 per cent. At high temperatures and (or) extensions, there is no internal evidence of such trouble, at any rate with the natural rubber compound employed in this work.

A series of eight sets of measurements was made on strips of this rubber. The first five, covering the range of extension from 11.4 to 79.4 per cent was made using strips about 25 mm. between marks, and temperatures of 44.9° C, 25.4° C, 0.0° C, the results are shown in Figure 5, in which χ is plotted as a

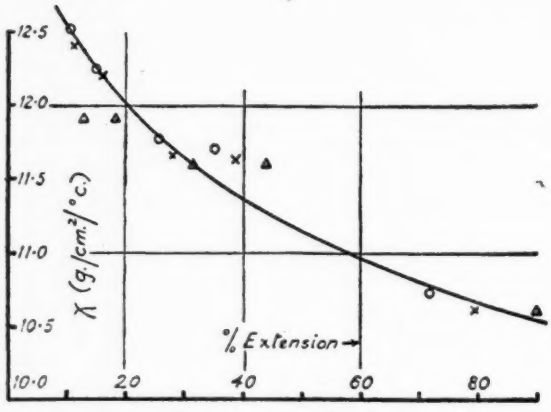

FIG. 5.—Temperature coefficient of elastic modulus for natural rubber A'. (⊙ 44.9° C, × 25.4° C, △ 0.0° C).

function of $\alpha = l/l_0$. Although there are irregularities between the different sets of measurements, it is clear that if these are eliminated by small vertical displacements, the 44.9 and 25.4° C data fall very nearly on the curve drawn. Indeed, within experimental error, χ evidently depends only on α. In an attempt to achieve higher precision at the lower elongations, longer strips (65 to 110 mm.) were employed, and the temperatures used changed to 50.0 and 19.9° C. The principal experimental difficulty was then found to lie in getting reproducible unstrained lengths. These were finally measured by hanging the strips, unloaded, in tubes and using the technique of alternate swelling and drying. Even so, the thermal expansion observed was not very reproducible, and was generally somewhat smaller than the usually accepted figure[8] of 2.2×10^{-4}. The volume expansivity was measured by a modification of Bekkedahl's method[9], and was found to be $6.7_0 \times 10^{-4}$. Unstrained lengths were therefore obtained by measuring them at 50° C (after swelling) and calculating the values at the lower temperature.

The final data are given in Table I, in which $\chi_T = -T\frac{\partial \chi}{\partial T}$ is the temperature-dependent part of χ. In calculating χ_T, data obtained at 0° C have been ignored, and the curve of Figure 5 employed to bring χ values measured at different temperatures to the same α.

TABLE I

TEMPERATURE DEPENDENCE OF χ

Series 1			Series 2		
	χ	χT		χ	χT
α	g./cm.²/° C		α	g./cm.²/° C	
1.114	12.4_0	-1.0	1.062	13.4_5	0.2
1.162	12.20	0.3	1.097	11.7_0	0.5
1.282	11.6_6	-0.3	1.193	11.6_7	0.8
1.388	11.6_5	0.3			
1.794	10.6_1	0.3			

The conclusion from these observations is that over the whole of this range the temperature dependence of χ is too small to measure with any certainty and cannot be large enough to change appreciably the form of dependence of χ on α.

Before accepting this as definitely established, a few measurements were made in another way, employing the apparatus described above for the stress-strain measurements. In this case the length of the specimen was kept constant by clamping the balance arm or by maintaining it in balance, while petroleum ether was introduced and then removed again in a stream of nitrogen. Working at temperatures of 40° and 20° C, results were less reproducible than with the previous method, but within the accuracy (about 1 per cent) with which χ could be measured, there was no indication that χ was temperature dependent. Since the temperature coefficients found in this way should err, if at all, in the direction of being too small, this is taken to afford strong confirmation of the previous result.

Some preliminary measurements on GR-S (rubber E), made *in vacuo* at constant load, gave results which agreed qualitatively with those of Roth and Wood[7] in showing χ_T to be negative and its arithmetical value to increase with extension.

The measurement of $\partial\chi/\partial T$ for swollen rubbers has proved still more difficult, and although no evidence was found that χ was temperature dependent, the accuracy attained was insufficient to warrant any definite conclusion. We cannot therefore entirely rule out the possibility that the greater constancy of χ for swollen rubbers arises from a temperature-dependent term χ_T whose variation with α fortuitously cancels that of $(\chi - \chi_T)$. In view of the observation that the same limiting value of χ is obtained in a series of good swelling agents, this possibility seems rather remote, and it will be ignored in the following discussion.

THERMODYNAMICS OF HIGH ELASTICITY

(*a*) THEORETICAL

Elliott and Lippmann[10] have recently discussed the thermodynamics of rubber elasticity, and have pointed out errors in most of the earlier work. An alternative treatment[11], leading to results in substantial agreement with theirs, may be given as follows:

We consider a strip of rubber of length l and volume V supporting a tension f and a hydrostatic pressure P at temperature T. If E and S are the internal energy and entropy, then taking S, V and l as the independent variables necessary to specify the system, we have:

$$dE = TdS - PdV + fdl \qquad (1)$$

Introducing the heat content $H(= E + PV)$ and the Gibbs free energy $G(= H - TS)$ equation (1) may be transformed to:

$$dG = -SdT + VdP + fdl \tag{2}$$

i.e.,

$$(\partial G/\partial T)_{P,l} = -S; \qquad (\partial G/\partial P)_{T,l} = V; \qquad (\partial G/\partial l)_{T,P} = f \tag{3}$$

Further,

$$(\partial H/\partial l)_{P,T} = (\partial G/\partial l)_{P,T} + T(\partial S/\partial l)_{P,T}$$

Substituting for S from (3) and using the identity:

$$\partial/\partial x \cdot \partial y/\partial z \equiv \partial/\partial z \cdot \partial y/\partial x$$
$$(\partial H/\partial l)_{P,T} = f - T(\partial f/\partial T)_{P,l} \tag{4}$$

We now define the deformation ratio α by writing[12]:

$$l = \alpha l_0\{1 + \beta(T - T_0)\} \tag{5}$$

where l_0 is the unstretched length at temperature T_0, and β is the coefficient of linear expansion of the unstretched rubber, *i.e.*, $3\beta V = (\partial V/\partial T)_{P_{1f=0}}$. We then have:

$$(\partial f/\partial T)_{P,\alpha} = (\partial f/\partial T)_{P,l} + (\partial f/\partial l)_{P,T} \cdot (\partial l/\partial T)_{P,\alpha} = (\partial f/\partial T)_{P,l} + \beta l(\partial f/\partial l)_{P,T}$$

whence,

$$(\partial H/\partial l)_{P,T} = f - T(\partial f/\partial T)_{P,\alpha} + \beta lT(\partial f/\partial l)_{P,T} \tag{6}$$

If the elongation is carried out at constant volume, instead of constant pressure, a similar analysis, using the Helmholtz free energy $F(= E - TS)$ instead of G, leads to:

$$(\partial F/\partial T)_{V,l} = -S; \qquad (\partial F/\partial V)_{T,l} = -P; \qquad (\partial F/\partial l)_{T,V} = f \tag{7}$$

and

$$(\partial E/\partial l)_{V,T} = f - T(\partial f/\partial T)_{V,l} \tag{8}$$

The relation between extensions at constant P and constant V is derived by combining (4) and (8) to give:

$$(\partial H/\partial l)_{P,T} - (\partial E/\partial l)_{V,T} = T\{(\partial f/\partial T)_{V,l} - (\partial f/\partial T)_{P,l}\}$$

This may be transformed by means of mathematical identities to:

$$(\partial H/\partial l)_{P,T} - (\partial E/\partial l)_{V,T} = T(\partial f/\partial l)_{P,T}(\partial l/\partial V)_{f,T} \cdot \frac{(\partial V/\partial P)_{T,f}}{(\partial V/\partial P)_{T,l}} \cdot (\partial V/\partial T)_{P,l} \tag{9}$$

Equation (9), although exact, is of little value as it stands, but consideration of the physical nature of the extension process enables the form for small extensions to be derived. Considering the terms on the right of Equation (9) the following conclusions may be drawn:

(1) If the stretched rubber is isotropically compressible, $(\partial l/\partial V)_{f,T} = l/3V$, and this is the limiting value as $f \to 0$. Volume changes clearly occur, largely by alterations of the distance between chains so that, for finite extensions, molecular orientation makes the compressibility in the direction of stretch less than that at right angles. It follows that, in general, $(\partial l/\partial V)_{f,T} \leqslant l/3V$.

(2) It will be shown later that f is almost independent of V at constant l, so the isothermal compressibilities at constant f and at constant l must be very nearly equal, *i.e.*:

$$(\partial V/\partial P)_{T,f} = (\partial V/\partial P)_{T,l}$$

(3) If the coefficient of thermal expansion of the stretched rubber is approximately the same as that of the unstretched:

$$(\partial V/\partial T)_{P,l} \simeq 3\beta V$$

Holt and McPherson[13] have shown $(\partial V/\partial T)_{P,l}$ to increase somewhat with extension, but the increase is quite negligible for extensions of <100 per cent. From these considerations, it is clear that Equation (9) may be written:

$$(\partial H/\partial l)_{P,T} - (\partial E/\partial l)_{V,T} \simeq \beta l T(\partial f/\partial l)_{P,T} \tag{10}$$

Combining with (6):

$$(\partial E/\partial l)_{V,T} \simeq f - T(\partial f/\partial T)_{P,\alpha} \tag{11}$$

This equation, which is only exact in the limit of small deformations, is equivalent to Elliott and Lippmann's conclusion. The above discussion suggests that approximation (1) is the least precise, so Equation (11) probably somewhat overestimates $(\partial E/\partial l)_{V,T}$.

(*b*) DISCUSSION OF THE EXPERIMENTAL DATA

The conclusion from the experimental section was that

$$\chi\left[= \frac{f}{TA_0(\alpha - 1/\alpha^2)} \right]$$

is substantially independent of T for a pure-gum natural rubber compound extended >100 per cent at constant pressure, so over this range: $f = T(\partial f/\partial T)_{P,\alpha}$. It follows from Equation (6) that

$$(\partial H/\partial l)_{P,T} = \beta l T(\partial f/\partial l)_{P,T}$$

which is equivalent to

$$(\partial H/\partial \alpha)_{P,T} = (\beta/\alpha) l^2 T(\partial f/\partial l)_{P,T}$$

We have also from Equation (3) $(\partial G/\partial \alpha)_{P,T} = fl/\alpha$ and thence:

$$T(\partial S/\partial \alpha)_{P,T} = (\partial H/\partial \alpha)_{P,T} - (\partial G/\partial \alpha)_{P,T}$$

The thermodynamic data given in Figure 6 were obtained in this way, using a smoothed plot of $(\partial f/\partial l)_{P,T}$. It also follows from Equation (11) that $(\partial E/\partial l)_{V,T} \simeq 0$, at least in the limit for small extensions. Now it is readily seen[14] that $(\partial H/\partial l)_{P,T}$ is very nearly equal to $(\partial E/\partial l)_{P,T}$ under the experimental conditions employed. The conclusion to be drawn is that on extension the volume of the rubber changes, and that the observed increase in the internal energy of the rubber is associated entirely with this volume change, at any rate for small extensions.

The magnitude of the volume change can be estimated, at least approximately, from the known dependence of the internal energy of rubber on isotropic changes of volume. For this we use the well known expression[15]:

$$(\partial E/\partial V)_T = 3\beta T/K \tag{12}$$

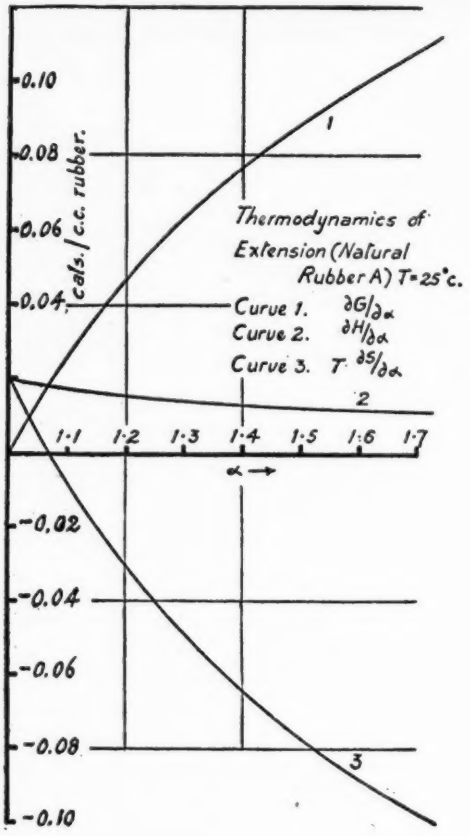

FIG. 6.

where $K = -(\partial ln V/\partial P)_T$ is the isothermal compressibility and for natural rubber is equal[8] to 5.1×10^{-5} bars^{-1}. Thus, assuming that the isothermal change of E with V is the same whether a hydrostatic pressure or a unidirectional tension is applied, it is readily seen that the expansion ΔV produced by extending the rubber to length l is given by:

$$\Delta V = \frac{K}{3\beta T}\int_{l_0}^{l}\left(\frac{\partial E}{\partial l}\right)_{P,T}\cdot dl \qquad (13)$$

where l_0 is the unstrained length of the rubber at temperature T. With our experimental value of $(\partial E/\partial l)_{P,T}$ this becomes:

$$\Delta V = \frac{K}{3}\int_{l_0}^{l} l\left(\frac{\partial f}{\partial l}\right)_{P,T} dl \qquad (14)$$

Values of ΔV calculated from Equation (14) are given in Figure 7 (*a*) and show that a 70 per cent extension of the rubber must be accompanied by a bulk expansion of about 0.01 per cent. This expansion was not detected by Holt and

McPherson[13] in their careful study of the volume changes produced on extension, but there is no necessary discrepancy in this fact, since the predicted expansion is very close to the limit of their experimental accuracy.

Calculation of the volume changes accompanying larger extensions is only possible on the assumption that the change in internal energy arises from volume changes equivalent to those produced on the unstrained rubber by a hydrostatic pressure. With this assumption, Equation (10) has been used to calculate ΔV from the data on natural rubber of Wood and Roth[7], and in Figure 7 (*b*) the results are compared with Holt and McPherson's experimental measurements. Bearing in mind that ΔV is not the same function of α for all rubbers, the comparison suggests that the most important energy changes on extension are associated with volume changes.

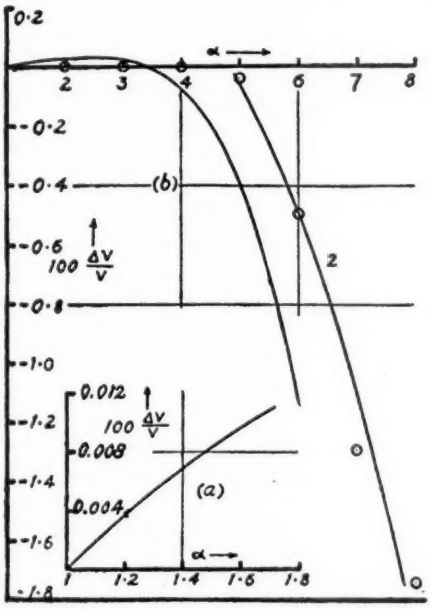

FIG. 7.—Volume changes on extension of natural rubber. (*a*) (Inset). Calculated from Equation (14). (*b*) 1. From Roth and Wood[7], using Equation 13. 2. Data of Holt and McPherson[13].

Roth and Wood's data[7] for GR-S, which we have qualitatively confirmed, show that in general $f \neq T(\partial f/\partial T)_{P,\alpha}$, so the energy changes on extension are not necessarily wholly associated with volume changes. It is, however, to be noted that these data give the limiting value of $(\partial H/\partial l)_{P,T}$ as $\alpha \to 1$ as $\beta l T(\partial f/\partial l)_{P,T}$, and therefore $(\partial E/\partial l)_{V,T} \to 0$.

Figure 6 shows that small extensions at constant pressure are accompanied by an increase of entropy, but that for larger extensions $(\partial S/\partial\alpha)_{P,T}$ becomes negative. To determine how far the entropy of extension depends on the volume, it is convenient to consider the effect of volume changes on the tension in a strip of rubber held at constant length and temperature. Suppose a strip of rubber of volume V_0 is extended isothermally at constant P to a length l, its tension then being f and its volume $V_0 + \Delta V$. A hydrostatic pressure is

then applied so as to reduce the volume to V_0, without change of l. The resulting increase of tension Δf will be given by:

$$\Delta f = -(\partial f/\partial V)_{l,T}\cdot\Delta V = (\partial f/\partial l)_{V,T}\cdot(\partial l/\partial V)_{f,T}\cdot\Delta V \qquad (15)$$

Now, for small extensions, $(\partial l/\partial V)_{f,T} \simeq l/3V$, and $(\partial f/\partial l)_{V,T}$ does not differ very significantly from $(\partial f/\partial l)_{P,T}$, so:

$$\Delta f \simeq \tfrac{1}{3}l(\partial f/\partial l)_{P,T}\cdot\Delta V/V \qquad (16)$$

Inserting values, it is easily shown that $\Delta f \ll f$. Thus, for the limit of small extensions, combination of Equations (14) and (16) leads to:

$$(\Delta f/f)_{f\to 0} = Kl_0^2(\partial f/\partial l)_{f=0}/9V_0 \qquad (17)$$

which is about 0.007 for the natural rubber compound used in this work.

Since we have:

$$\begin{cases} T(\partial S/\partial l)_{P,T} = (\partial H/\partial l)_{P,T} - f \\ T(\partial S/\partial l)_{V,T} = (\partial E/\partial l)_{V,T} - f \end{cases}$$

where f has now been shown to be substantially the same whether measured at constant P or at constant V, it follows that:

$$T\{(\partial S/\partial l)_{P,T} - (\partial S/\partial l)_{V,T}\} \simeq (\partial H/\partial l)_{P,T} - (\partial E/\partial l)_{V,T} \qquad (18)$$

In other words, the increase of internal energy associated with the expansion which accompanies isothermal extension is almost exactly balanced by an equivalent increase of entropy, leaving the tension practically the same as if expansion had been prevented by applying a hydrostatic pressure.

ORIGIN OF VOLUME AND ENERGY CHANGES

The volume and energy changes revealed by the foregoing thermodynamic analysis could arise in a variety of ways. Of these, the one which seems almost certain to be the dominant effect at low extensions is related to the hydrostatic component of the applied tension. Following the classical theory of small elastic deformations, the applied force may be resolved into shear stresses which change the shape of the material without affecting its volume, and a hydrostatic component which changes the volume but not the shape. Now the hydrostatic component of a unidirectional force is a tension $-\Pi$ equal in magnitude to one-third of the tensile stress[12], *i.e.*:

$$\Pi \simeq -\tfrac{1}{3}fl/V \qquad (19)$$

The tension acts on the material in substantially the same way as an externally applied hydrostatic tension of equal magnitude would act on the undeformed rubber, so the resulting expansion ΔV is $-\Pi KV$, or

$$\Delta V \simeq \tfrac{1}{3}Kfl \qquad (20)$$

Equation (20) is identical with the limiting form of Equation (14) as $l \to l_0$. We conclude, therefore, that for small extensions, the observed expansion is produced by the hydrostatic component of the tensile force. It consists of an increase in the average intermolecular spacing, and is accompanied by equivalent increases in both internal energy and entropy.

Other mechanisms which must come into play at higher extensions are discussed below, but none of them can at present be treated quantitatively.

(1) Changes in packing arise from molecular orientation, leading ultimately in some cases to crystallization; these involve reductions of volume with consequent reductions in both E and S.

(2) Another type of change of packing which may be significant for any inhomogeneous rubber is akin to the mixing of liquids. Thus, if the rubber chain is made up of two types of unit, as in a copolymer, both the energy and entropy of the system depend on the relative arrangements of adjacent chains, and may therefore change on extension, even at constant volume. This effect may of course occur even with a natural rubber vulcanizate, the sulfur atoms representing the second structural unit. It is clear that the total energy of the rubber depends to a very considerable extent on the average number of S-S contacts, but this is probably not very dependent on the extension.

(3) For very large extensions, bond deformations may occur to a slight extent; the resulting increases of energy and entropy could of course be very large, without the volume being greatly affected.

Of these three possibilities, (1) is certainly important, (2) is rather difficult to evaluate, and (3) is probably negligible until tensions of the order of the tensile strength are reached. In all of them it is clear that any change in energy is at least partly balanced by a corresponding entropy change, leaving the tension approximately the same as if all these complications could be avoided.

THE STATISTICAL THERMODYNAMICS OF HIGH ELASTICITY

Attempts to calculate the free energy of extension statistically[3] are based on the model of a vulcanized rubber as a network of chains each made up of freely rotating links having length and direction but no volume. The internal energy of the system is therefore not taken into account at all, and the tension is described in terms of the decrease of entropy on extension[16]. The general equation for the tension in a strip of rubber swollen until the volume fraction of rubber is v_r has been given by Flory[2]:

$$f = \rho_r A_0 RT/M_c(l/l_0 - l_0^2/l^2 v_r) \qquad (21)$$

where ρ_r is the density of the rubber, and M_c the mean molecular weight between adjacent junction points of the network. The parameter χ used in this paper should therefore be a constant, equal to $R\rho_r/M_c$. Figures 1 and 2 show that this equation fails to describe accurately the variation of f with either l or v_r but becomes increasingly successful as the rubber is progressively swollen.

In seeking to explain these discrepancies, account must be taken of the thermodynamic data which have been discussed above. These show that energy and entropy changes occur on extension which are to be understood in terms of the fluid properties of the rubber, but that these largely cancel, leaving the tension unchanged. It is clear therefore that, although Equation (21) is derived from the calculated entropy of extension, it is much more appropriate to compare the theoretical value with the experimental f than with $-T(\partial S/\partial l)_{P,T}$ as some earlier workers have done[5]. Departures from the theoretical dependence of f on α are most marked for small extensions[17] and become less as the rubber is swollen, finally becoming very small. The fact that Equation (21) is obeyed by highly swollen rubbers at small extensions makes it natural to regard this as the ideal behavior, and to look for an explanation of the anomalous elastic properties of unswollen rubber. The thermodynamic analysis shows that the anomaly is in no way associated with the observed

volume change, nor with any process involving energy changes on extension. It would seem that the only type of explanation consistent with the data is that the statistical calculations underestimate the extent to which the number of configurations of dry rubber is reduced by extension, while giving correctly the corresponding figure for a swollen rubber. This may be understood by considering the probable molecular structure of the rubber. It is well known that in liquids consisting of long molecules, there is a marked tendency for parallel alignments. This is shown *e.g.*, in the relatively high melting points of *n*-paraffins (surprising in view of the very low intermolecular forces) and in the high entropies of evaporation of *n*-paraffins as short as hexane, heptane and octane[18]. Natural rubber at room temperature is in the temperature range in which crystallization readily occurs[19], and there is every reason to suppose that in the normal structure of amorphous rubbers there is extensive local alignment of portions of adjacent chains. Since it has been shown that the energy changes for small extensions are quantitatively related to the calculated ex-

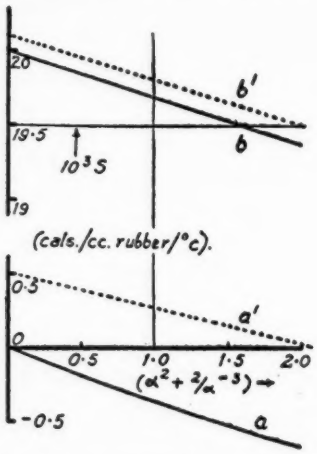

FIG. 8.—Entropy changes on extension (schematic). *a*, *a'* dry rubber. *b*, *b'* swollen 100 per cent. Dotted curves theoretical.

pansion, there can be no large changes of alignment in this region. This alignment must diminish the configurational entropy of the rubber before and after stretching; the experimental data suggest strongly that this decrease becomes progressively greater as the rubber is extended. It is consistent with this view that swelling the rubber, which will break down the alignment, is found to make the elastic behavior more ideal. Figure 8 shows schematically the entropy changes on extension and swelling at constant volume compared with the theoretical curves. The entropy is plotted as a function of $(\alpha^2 + 2/\alpha - 3)$ for dry and swollen rubbers. The theoretical plots, shown dotted are linear[2], their slopes having the ratio $1 : v_r^{-\frac{1}{3}}$. The experimental results (full lines) show a curvature much more marked in the dry rubber. In accordance with the above argument the theoretical lines are drawn higher than the experimental; the displacement represents the entropy of alignment and is of course unknown but it should be less for the swollen rubber than for the dry. Insertion of the limiting value of χ found for swollen rubbers in Equation (21) is thus considered to give the best available estimate of the

molecular weight between junction points. For rubber A, *e.g.*, this gives a value of $M_c = 8.4 \times 10^3$, which may still require correction, as Flory has pointed out,[20] for the effects of network imperfections such as the looping together of chains, and the existence of loose ends.

The difference in the entropies of the unstretched rubbers represents the entropy of swelling, and is an estimated figure. It is clear from this hypothesis that the experimental entropy of swelling should be greater than the theoretical value, at any rate at small extents of swelling, and might conceivably be used to estimate the entropy of alignment. In the only case for which really reliable data are available, namely natural rubber and benzene[1], this is found to be the case, but this may well be partly due to a breakdown of the benzene structure. There is, however, some evidence of similar behavior for most of the liquids for which provisional estimates of the entropy of swelling are available in this region[21].

The final conclusion is therefore that both the elasticity and the swelling of rubbers is influenced to a considerable extent by the structure of the rubber, and that a plausible qualitative explanation can be given in terms of local molecular alignments.

Appendix

Composition of Rubbers Used*

Rubber (100)	A, A′ Natural (Smoked Sheet)	B Neoprene-GN	C Thiokol-FA	D Buna-N	E GR-S
Sulfur	2	—	—	1.5	2
Zinc oxide	2	1	5	5	5
Magnesium oxide	—	4	—	—	—
Stearic acid	0.5	0.25	1	1	1
Benzothiazyl disulfide	1	—	0.35	1	1
Diphenylguanidine	—	—	0.1	—	0.25
Di-*o*-tolylguanidine	—	0.5	—	—	—
Nonox	0.5	2.0	—	—	—
Vulcanization (min.)	45	30	50	30	45
(Temp. ° C)	142	142	148	142	142

* A and A′ differed in the degree of milling before cure, A′ being more highly milled and therefore of lower molecular weight.

SUMMARY

Measurements of the effect of extension on tension are reported for rubbers, both dry and swollen, to various extents in a range of liquids. According to the current statistical theory a quantity χ, defined by:

$$f/TA_0(l/l_0 - l_0^2/l^2v_r)$$

should be a constant for a given rubber. Experimentally χ is found to fall with increasing extension, or on swelling, but to tend ultimately to a limiting value independent of the nature of the liquid, and (within limits) of the degrees of swelling and extension.

A new experimental and theoretical discussion of the thermodynamics of elasticity shows that small extensions result in an increase of internal energy, which arises from an expansion of the rubber and is in no way connected with the observed variations of χ. These are attributed to a local ordering of the rubber, which is broken down by swelling. The limiting value of χ for swollen rubbers should be employed in calculating the degree of cross linking from the tension.

ACKNOWLEDGMENT

The author's thanks are due to S. C. Stokes for preparing the rubbers used, to (Miss) J. Ferry for experimental assistance, and to R. S. Rivlin and L. R. G. Treloar for many valuable discussions. The work described forms part of the program of fundamental research in rubber undertaken by the Board of the British Rubber Producers' Research Association.

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[11] This analysis is an obvious extension of that given by Guggenheim ("Modern Thermodynamics", p. 11) for isotropic systems.
[12] More precisely, $(\partial l/\partial T)_{P,\alpha} = \beta l$, and $(\partial l/\partial \alpha)_{P,T} = l/\alpha$.
[13] Holt and McPherson, *J. Research Natl. Bur. Standards* **17**, 657 (1936).
[14] $(\partial H/\partial l)_{P,T} = (\partial E/\partial l)_{P,T} + P(\partial V/\partial l)_{P,T} = \{(\partial E/\partial V)_{P,T} + P\}(\partial V/\partial l)_{P,T}$. $(\partial E/\partial V)_{P,T}$ is an "internal pressure", and therefore of the order of 10^3 atmospheres, so the term in P is completely negligible unless a very large hydrostatic pressure is applied. It is to be noted that $(\partial H/\partial l)_{V,T} \neq (\partial E/\partial l)_{V,T}$.
[15] Love, "Mathematical Theory of Elasticity", p. 83.
[16] This is not quite true; James and Guth (*J. Chem. Physics* **11**, 455 (1943)) use a model in which the network exerts a tension on the bounding surfaces of the rubber, which must be balanced by an increase in the internal pressure of the material. This internal pressure would diminish as the rubber is stretched and thus give rise to a bulk expansion and an increase of internal energy. For small extensions, $(\partial E/\partial l)_{\beta,T}$ estimated in this way is consistent with the value obtained from the perfectly general considerations of this paper. For higher extensions, their analysis is not in accord with the present data.
[17] A different type of deviation occurring at high extensions where χ increased rapidly with α has been discussed by James and Guth (*J. Chem. Physics* **11**, 455 (1943)) and by Treloar (*Trans. Faraday Soc.*, in press).
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MODIFICATIONS OF CHLORINATED RUBBER BROUGHT ABOUT BY SOME ORGANIC BASES. PIPERIDINE *

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INTRODUCTION

By virtue of certain characteristics, among others its resistance to chemical reagents, which is one of its most valuable properties, chlorinated rubber has already found a wide field of applications. It is curious, however, that some materials which are only slightly corrosive are capable of affecting it, *e.g.*, water and certain organic bases, the basicities of which are considerably lower than the basicity of potassium hydroxide or of sodium hydroxide.

PREVIOUS PUBLISHED WORK

The first patent which deals with the action of organic bases on chlorinated rubber was taken out in 1937[1]. This patent covers organic bases having dissociation constants of the order of 10^{-5}, such as methylamine, dimethylamine and trimethylamine, which insolubilize chlorinated rubber and harden it in a way somewhat comparable to the effect of vulcanization on ordinary rubber.

Other patents refer to the same type of transformation brought about by somewhat different compounds, *e.g.*, dithiocarbamates, thiuram sulfides, and hexamethylenetetramine, in patents of the Raolin Corporation[2], and polyamines in certain German patents[3].

The only scientific study which has been published on this type of reaction is a paper by Lichtenberger and Naftali[4]. By heating chlorinated rubber in pyridine solution for several hours on a steam bath, gelation takes place rapidly, with dichlorohydration and formation of pyridine hydrochloride. In cold dilute solution the reaction proceeds much more slowly, with partial gelation only after 1,100 hours. Under these particular conditions evidence was obtained of the formation of a quaternary salt of pyridinium chloride.

It is interesting to compare these results with the fact pointed out by Frydlender[5] that paints made of chlorinated rubber undergo in time internal transformations whereby they become brittle, progressively less soluble, and finally insoluble in all solvents.

From this brief survey of the published literature, it is evident that all these reactions of chlorinated rubber may be grouped on the one hand into those involving reagents which are relatively simple compounds from the chemical viewpoint, comprising basic organic compounds such as amines, and on the other hand, much more complex compounds having no significant relation to the former group of compounds, and functioning as accelerators of the vulcanization of rubber.

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* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 22, No. 3, pages 49–55, March 1945.

All these reagents have the same effects on chlorinated rubber, particularly in their ability to insolubilize chlorinated rubber by some still unknown reaction.

A more detailed study of these phenomena was therefore of interest, and the work described in the present paper was devoted chiefly to the action of piperidine, the effects of which on chlorinated rubber are very evident.

MODIFICATIONS BROUGHT ABOUT BY THE ACTION OF PIPERIDINE

When a small quantity of piperidine, *e.g.*, 5 per cent by weight of the chlorinated rubber, is added to a 20 per cent benzene solution of chlorinated rubber, the color of the liquid, originally clear yellow, becomes progressively browner, and then turbid, with formation of a crystalline precipitate composed of fine colorless needles; finally gelation takes place.

The appearance of the mixture varies with quantity of reagent added and with the time of the reaction. In particular, gelation is more or less strong and more or less rapid according to the proportion of reagent. Heat accelerates the insolubilization of the chlorinated rubber, as can be proved by repeating the experiment at the temperature of a steam bath.

To throw light on the cause of these transformations, and in what way piperidine reacts, the properties of the new modified chlorinated rubber were examined.

It may be assumed that two types of reactions take place.

(1) Combination of the base with chlorinated rubber, as Lichtenberger and Naftali[4] have shown to be true in the case of pyridine. Under these conditions the final product should increase in weight and should contain both chlorine and nitrogen.

(2) Dechlorohydration of the chlorinated rubber, *i.e.*, elimination of combined hydra acid by the piperidine. This last concept seems to be the more acceptable one, because, on the one hand, modified chlorinated rubber does not contain any nitrogen, has lost a certain percentage of combined chlorine, and weighs less than the original chlorinated rubber, and, on the other hand, the progressive formation of piperidine hydrochloride in the original mixture suggests that there is a change in structure somewhat comparable to that brought about by vulcanization.

Chlorinated rubber modified by the action of piperidine has new properties, which vary according to the operating conditions and in particular with the percentage of piperidine which has reacted. It acquires, both in the dry state and in solution, a more or less brown color, its hardness and friability are increased, and its thermoplasticity is reduced, its softening temperature being raised in some cases as much as 25 or 30° C.

When heated, a moulded disc of ordinary chlorinated rubber swells and its diameter increases (its apparent density equally); on the contrary, modified chlorinated rubber not only does not expand but actually undergoes a slight homothetic contraction. When chlorinated rubber has been treated with relatively small quantities of piperidine, the products remain soluble in ordinary solvents of chlorinated rubber, although the solutions do become more viscous. With higher proportions of piperidine, insoluble products are obtained. The effect of heat is to increase still more the insolubility of these products. It should be added that the stability is not increased. The modified product tends to be even less stable than the original product.

OTHER AMINES

Transformations similar to those which were obtained with piperidine have been obtained with other amines. The degree of the effect produced depends chiefly on the electrolytic dissociation constant, *i.e.*, on the basicity of these compounds.

Aniline, dimethylaniline, phenylhydrazine, pyridine, and quinoline, which are weak bases, bring about only relatively small modifications in chlorinated rubber, with separation of relatively little hydrogen chloride, whereas more highly basic compounds such as benzylamine, ammonia, triethanolamine, diethylamine, *n*-butylamine,and diethylenetriamine, give chlorinated rubber products which are modified to as great a degree as those resulting from the action of piperidine. Diethylenetriamine in particular insolubilizes chlorinated rubber very rapidly.

Some accelerators of vulcanization, such as hexamethylenetetramine and anhydroformaldehydeaniline, are effective modifying agents. In principle, then, it does not matter what basic compound is chosen to dechlorohydrate chlorinated rubber in solution. Practically, however it is necessary that the reagent be soluble in solvents for chlorinated rubber, and for this reason organic bases such as quaternary ammonium hydroxides or inorganic hydroxides, such as potassium hydroxide and calcium hydroxide, do not have the same effect.

POSSIBLE APPLICATIONS

The special properties shown by modified chlorinated rubber may be of interest for uses where ordinary chlorinated rubber is unsuitable because of its tendency to soften and swell when heated and because of its low resistance to solvents. The applications described in patents are concerned in most cases with coatings and insoluble adhesives; however, one should not in this case lose sight of the fact that the presence of compounds which are very soluble in water, *e.g.*, an excess of unreacted base, or hydrochloride of the amine, can impair the high resistance of these paints to water. By the use of chlorinated rubber from which these deleterious compounds have been removed by steam distillation or precipitation by a nonsolvent, this shortcoming can be avoided, and from an industrial viewpoint, treatment with an organic base can be pictured as an operation between the end of the chlorination process and separation of the solvent, so that the ordinary process of manufacture is not changed essentially.

The object of the investigation described in the present paper was not to approach the problem in a practical way but to contribute to a better theoretical understanding of a type of reaction which has been only lightly touched upon heretofore, yet which is open to practical applications. The attempt has been made to interpret rationally the results which have been obtained by falling back on general theories of the molecular structure of high polymers which have been found to be in accord with experimentally established facts.

THEORETICAL INTERPRETATION

The appearance of piperidine hydrochloride in a solution of chlorinated rubber to which piperidine has been added indicates a process of dechlorohydration, whereby the piperidine plays the part of the dechlorohydrating agent.

It is understandable, then, why the changes in properties of chlorinated rubber depend on the proportion of alkaline reagent added and on the electro-

lytic dissociation constant of the latter. The reaction, which tends to be quantitative with highly basic compounds like piperidine, is, on the contrary, very slow and incomplete with weakly basic compounds.

In this last case, the quantity of hydrogen chloride formed is sometimes so small that the combined chlorine contents of the chlorinated rubber before and after treatment are practically the same. This has led the author of a United States patent[2] to assume that the compounds in question (thiourea, hexamethylenetetramine, etc.) are not basic enough to withdraw chlorine from chlorinated rubber. However, if the secondary products of the reaction are examined carefully, it will be found that there is always a small amount of chlorine eliminated which is greater than in a blank test, and sometimes is only a few milligrams. This difference is never negligible, although too small to be detected by means of the percentage of combined chlorine in the chlorinated rubber.

The elimination in the form of hydracid of a part of the combined chlorine in chlorinated rubber should logically lead to the formation of incompletely chlorinated rubber. If the products differ from completely chlorinated rubber, they differ still more from incompletely chlorinated rubber, which is, for example, very thermoplastic[6]. We are, therefore, concerned with new products which may be regarded in their turn as being derivatives of chlorinated rubber and to which must be attributed a special structure different from that of the compounds from which they are derived. The dechlorohydration which is observed can be interpreted as a condensation reaction involving initially the least stable chlorine atoms, *i.e.*, those united to the carbon atoms carrying the methyl groups.

The greater the proportion of piperidine which has reacted with the chlorinated rubber, the lower the percentage of combined sulfur in the modified chlorinated rubber obtained. For example, the removal of one molecule of hydrogen chloride per isoprene group results in the formation of a chlorinated rubber, $C_5H_5Cl_3$, which contains not more than 62 per cent of combined chlorine. This is almost the same as the product obtained by treatment of ordinary chlorinated rubber with approximately 10 per cent of piperidine. A higher proportion of piperidine then removes more chlorine and hydrogen atoms, with formation of products progressively richer in carbon.

The liberation of hydrogen chloride does not involve the formation of double bonds because, as can be shown by determinations of the iodine number, the modified chlorinated rubber is almost saturated. It may, therefore, be assumed that the final product contains cyclic groups and intermolecular bridges, a type of structure which has been proposed by other investigators for practically identical reactions. First of all, with regard to cyclization reactions, Harries[7] has described the action of pyridine bases on rubber hydrochloride, which is characterized by the liberation of hydrogen chloride. Staudinger and Staudinger[8] took up this problem by studying the action of powdered zinc, and succeeded in cyclizing rubber, as indicated by viscosity measurements.

With regard to intermolecular bridges, Schweitzer[9] has advanced the idea that, when rubber is chlorinated, the double bonds resulting from the substitution reactions are capable of forming two-dimensional or three-dimensional networks which result in a more or less pronounced brown color of the product and an increase in viscosity even to the point of gelation, all of which phenomena have also been observed in the action of alkaline reagents on chlorinated rubber.

This type of reaction of chlorinated rubber with bases, including weak bases, shows that the inactivity of chlorinated rubber is not so complete as is

generally supposed, and that it actually behaves about like other organic chlorinated compounds.

In the future, then, a knowledge of these phenomena should be useful, particularly in avoiding bad results with chlorinated rubber paints.

CONCLUSIONS

Organic bases react with chlorinated rubber, liberate hydrogen chloride, and form new modifications of the chlorinated rubber. The reaction involves condensation, with the result that the products are less thermoplastic, swell less when heated, and are less soluble. It is obvious, then, that in spite of ordinary chlorinated rubber being resistant to very corrosive substances such as concentrated acids and caustic alkalies, it is attacked by much less aggressive substances. It may be assumed that still other compounds among those which might be regarded *a priori* as inactive actually show a notable activity. In any case, it is absolutely necessary to know their activity so as to avoid trouble when chlorinated rubber is used with materials of a wide variety of types.

EXPERIMENTAL PART

OPERATING TECHNIQUE

Separation of the product.—After treatment of the solution of purified chlorinated rubber with the organic base, the reaction mixture was steam-distilled. Under these conditions: (1) the solvent of the chlorinated rubber, which was benzene, and the excess base which had not reacted distilled, the amount of the latter being determined by an alkalimetric analysis of the distilled aqueous mixture, and (2) the chlorinated rubber remained behind in the distillation flask, and was separated by filtration of the aqueous solution; the hydrochloride of the base was extracted from this filtered solution. A convenient method for determining the quantity of this hydrochloride is to determine the ionized chlorine.

Technique used in the various measurements.—After drying the chlorinated rubber around 70° C, a pellet was moulded hot under pressure to measure the thermoplasticity, as already described by one of the present authors[6]. The expansion or contraction of the moulded disc was then measured by means of a slide caliper.

To determine the solubility, 100 milligrams of the product was treated in a test-tube with 3 cc. of pure benzene; after twenty-four hours 1 cc. of the supernatant liquid over the insoluble residue remaining on the bottom of the flask was decanted and evaporated to dryness in a tared crystallizing dish; the weight of the dry residue, multiplied by three, is regarded as the percentage of soluble phase.

The percentage of combined chlorine in the chlorinated rubber was determined by the Volhard method after mineralization by fusion with an alkali (the alkaline mixture, composed of 1 part of potassium nitrate, 1 part of potassium carbonate, and 2 parts of sodium carbonate, was added to the product either swollen or dissolved in benzene).

INFLUENCE OF THE MOST IMPORTANT FACTORS

Proportion of piperidine and time of the reaction (see Table 1).—Irrespective of the proportion of piperidine, the reaction is almost complete after five days at room temperature.

The maximum decrease in thermoplasticity passes through an optimum point which corresponds to 20 per cent of the reagent for a time of reaction of five days. The expansion brought about by heating chlorinated rubber which has been treated with small percentages of piperidine is reduced greatly and becomes negligible with about 3 per cent of piperidine. Above 3 per cent of this base, the product contracts and its density increases.

In determining solubility, measurements were made of the same product before and after the heating necessary for measuring its thermoplasticity. The solubility decreases in proportion to the proportion of piperidine and with the time of treatment; moreover, the solubility of any given product is decreased by heating.

The percentage of combined chlorine in modified chlorinated rubber is always lower than that of the original untreated chlorinated rubber, as was to be expected.

TABLE 1

EFFECTS OF THE TIME OF REACTION AND THE PROPORTION OF PIPERIDINE ON THE PROPERTIES OF CHLORINATED RUBBER

Time of reaction (days)	Piperidine (percentage based on chlorinated rubber)	Appearance of mixture	Alkalinity (cc. of 0.1 N H_2SO_4)	Chlorine ionized (mg.)	Softening temperature (° C)	Swelling (+) or shrinkage (−)	Solubility		Combined chlorine) (percentage
							Before heating	After heating	
	Control	Yellow solution	0.1	2.2	126	+5	100	100	65.3
	0.3	Orange solution	0.1	2.2	132	+3	100	100	65.3
	2	Brown solution	1.4	2.7	135	+1	100	96	64.3
	5	Slightly turbid brown solution	5.7	17	140	−1.7	99	78	64.3
0	10	Turbid brown solution	16	20.3	150	−2	98	59.5	64.3
	20	— —	30.5	22	152	−2.8	96	57	62.7
	50	Turbid, rapid precipitation	83.5	43.3	155	−3	75	21.5	60.2
	100	— —	156	51.2	160	−3.2	54	10	57.5
	Control	Yellow solution	0.1	2.2	125	+8	100	100	65.4
	0.3	Brown solution	0.1	2.5	130	+5	100	100	65.3
	2	Turbid	0.3	6.7	137	+3	100	81	63.8
1	5	Crystalline precipitate	1.2	25.2	142	−2.8	85.5	60	63.5
	10	— —	2.6	32.4	150	−2	57	35	61.8
	20	Crystalline precipitate	9	79.3	156	−2.2	56	15	57.3
	50	— —	36	162	152	−2.8	22.5	4	48
	100	— —	81	284	142	−2.2	9	1	35.7
	Control	Yellow solution	0.1	2.1	125	+7.5	100	100	65.2
	0.3	Slight deposit	0.1	2.1	135	+2	100	100	65.3
	2	Precipitate	0.3	6.7	137	+1.5	99.5	81	64.5
5	5	Abundant precipitate	0.6	32	150	−1.7	70	53	63.4
	10	Very abundant precipitate	1.2	47.5	152	−2	59.5	30	61
	20	Precipitation with complete gelation	2.5	103	160	−1.9	38	18	57.9
	50		5.3	210	140	−2	33	4	44.2
	100		25.4	540	135	−2.5	18	1	29.4
	Control	Yellow solution	0.1	0.9	122	+7	100	100	65.5
	0.3	Slight deposit	0.1	2.8	135	+1	100	99	65.3
12	2	Precipitate	0.2	8	141	−1	98	75	64.9
	5	Abundant precipitate	0.5	25.6	150	−2	77	53	62.8
	10	Very abundant precipitate	0.8	30.6	155	−2	69	32	60
	20	Precipitation and gelation	1	48	162	−2	43	9	55.2
	Control	Yellow solution	0.1	1.4	126	+2.2	100	100	65.6
	0.3	Slight deposit	0.1	1.3	137	+0.2	100	100	65.3
29	2	Precipitate	0.2	7.1	150	−2	95	68	64.7
	5	Abundant precipitate	0.3	18.1	153	−1	70	50	62.5
	10	Very abundant precipitate	0.6	34.4	160	−2.2	62	30	59.8
	Control	Yellow solution	0.1	3.7	125	+6	100	100	65.4
	0.3	Slight deposit	0.1	4.8	140	−0.5	100	96	65.2
48	2	Precipitate	0.1	13.8	150	−1	98	73	64.4
	5	Abundant precipitate	0.2	19.9	154	−2	80	46	61.4
	10	Precipitation and gelation	0.2	49	156	−1.8	41	28	60.8

In general, the alkalinity, ionized chlorine, solubility, and combined chlorine are functions of the quantity of piperidine and of the time of treatment. With increase in piperidine, the thermoplasticity passes through a minimum, and swelling by heating decreases, becomes negligible, and finally becomes a contraction.

Concentration of chlorinated rubber.—The rapidity of gelation of a solution increases with increase in the concentration of chlorinated rubber in the solution. At the same time, the solubility and the percentage of combined chlorine in the product decrease. It may accordingly be assumed that the concentration of chlorinated rubber influences the rate of the reaction.

Nature of the solvent.—The reaction was carried out in benzene, xylene, chloroform, and carbon tetrachloride. The appearance of the mixtures differed according to the solubility of the secondary product. The best results were obtained with benzene and chloroform. Because of its being less volatile, xylene was more difficult to eliminate completely by steam-distillation, and carbon tetrachloride is a poor solvent for chlorinated rubber.

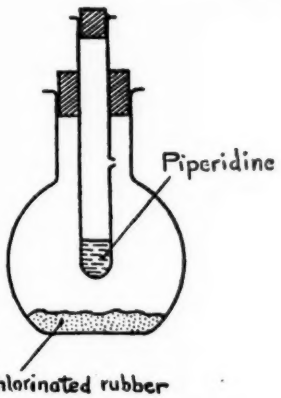

FIG. 1.—Apparatus for the treatment of chlorinated rubber with piperidine.

The presence of water does not interfere with the reaction, and this is of interest in connection with aqueous emulsions of chlorinated rubber for paints, which may contain, as emulsifying agents, basic compounds, such as triethanolamine.

Finally, in the absence of a solvent, the reaction progresses in the same way. It is sufficient, for example, to expose chlorinated rubber in powder form to piperidine vapor (see Figure 1) to modify profoundly its properties; in this case it is possible to eliminate by simple washing with water the piperidine hydrochloride which the product retains.

Effect of heat.—The effect of heating a solution of chlorinated rubber containing 5 per cent of piperidine on a steam bath is to accelerate the reaction to a very rapid rate during the first half-hour. The thermoplasticity and swelling of the product are thereby modified to the extent brought about by carrying on the reaction for five hours at ordinary temperature. Likewise the solubility and percentage of combined chlorine decrease progressively with the time of heating.

Nature of the basic compound.—Table 2 gives, in the order of decreasing effectiveness, the amines which were tested in the proportion of 5 per cent (by

weight of the chlorinated rubber) with 10 cc. of a 20 per cent benzene solution of chlorinated rubber for five days in the cold.

TABLE 2

THE PART PLAYED BY BASES OF DECREASING EFFECTIVENESS IN THE DECHLOROHYDRATION OF CHLORINATED RUBBER

No.	Organic base	Electrolytic dissociation constant (K)	Weight of chlorine lost by treatment (mg. of chlorine per 1.8 g. of chlorinated rubber)
1	Piperidine	1.6×10^{-3}	34.1
2	Diethylamine	1.2×10^{-3}	36.4
3	Ethylenediamine	7.4×10^{-5}	39
4	Diethylenetriamine	—	17.4
5	*n*-Dibutylamine	—	18.6
6	Benzylamine	2.4×10^{-5}	20.6
7	Ammonia	2.3×10^{-5}	18.5
8	Triethanolamine (technical)	—	14.2
9	Pyridine	2.4×10^{-9}	10.3
10	Phenylhydrazine (technical)	1.6×10^{-9}	6.4
11	Aniline	5.3×10^{-10}	6.4
12	Quniline	6.3×10^{-10}	5.7
13	Dimethylaniline (technical)	2.5×10^{-10}	3.5
14	Control	—	2

Strong bases tend to be neutralized quantitatively by chlorinated rubber and, in judging their effectiveness in the dechlorohydration of rubber, consideration must be given also to their effect in gram-equivalents.

Chlorinated rubber was made to react with ammonia by saturating benzene with this gas, and then mixing this solution (3.5 grams of ammonia per liter) with a solution of chlorinated rubber. Under these conditions the results were almost identical with those obtained by passing ammonia gas directly into a solution of chlorinated rubber.

With only 5 per cent by weight of the chlorinated rubber, diethylenetriamine increases progressively the viscosity of a solution of chlorinated rubber to a point where gelation is uniform and complete after a few days. On the contrary, at the same concentration, weakly basic amines, such as Nos. 9, 10, 11, 12 and 13 in Table 2, act very slowly; the reaction is never complete, and an excess of base always remains. With these particular bases, the appearance of the mixtures and the solubility remain practically unchanged, and the reductions in percentage of combined chlorine in the chlorinated rubber are rather small.

The effects of four vulcanization accelerators were likewise studied. Those chosen were hexamethylenetetramine, anhydroformaldehydeaniline, tetramethylthiuram disulfide, and mercaptobenzothiazole. Only the first two of these reacted well with chlorinated rubber under the particular conditions employed. The action is probably due to their slight alkalinity or perhaps (particularly under hot conditions) to decomposition products comprising among others, ammonia from hexamethylenetetramine and aniline from anhydroformaldehydeaniline, in other words two compounds already tested, as shown in Table 2.

It should be noted again that bases which are insoluble in solvents of chlorinated rubber, *e.g.*, potassium hydroxide, sodium hydroxide, and quaternary ammonium hydroxide, are practically inactive, even in the form of aqueous emulsions.

The work which has been described shows that chlorinated rubber can be modified so as to obtain: (1) products which are only slightly thermoplastic but are soluble; (2) products which are only slightly thermoplastic and are insoluble, and (3) products which are thermoplastic but are insoluble.

A SPECIAL STUDY OF PRODUCTS OBTAINED UNDER REPRESENTATIVE CONDITIONS

Four products were prepared—about thirty grams each—under different conditions, and were used to study the reaction in a quantitative way and thereby to examine in more detail the products of the reaction. These four preparations were the following.

(1) Chlorinated rubber, in the form of a 20 per cent solution in benzene, treated with 5 per cent by weight of piperidine for 30 minutes at 90° C.

(2) Chlorinated rubber, in the form of a 20 per cent solution in benzene, treated with 5 per cent by weight of piperidine for 5 days at room temperature.

(3) Chlorinated rubber, in the form of a 20 per cent solution in benzene, treated with 20 per cent by weight of piperidine for 5 days at room temperature.

(4) A control solution, comprising a 20 per cent benzene solution of chlorinated rubber, to which no piperidine was added.

After elimination of the excess of piperidine and solvent by steam distillation, there remained in the distillation flask, in addition to the precipitate of chlorinated rubber, a light yellow aqueous solution, which, by evaporation, left a solid residue containing chlorine and nitrogen. The quantity of this residue depended on the quantity of piperidine which had reacted. Since the percentages of ionized chlorine were almost identical in the three cases (values of 29.4 to 30.8), this dry residue represented a definite product, the most probable compound being piperidine hydrochloride, which contains 29.3 per cent of chlorine. The slightly higher values which were found experimentally may be attributed to the presence of impurities in the original chlorinated rubber, since the dry residue of the control sample was not negligible.

The next step was to purify this residue and to compare it with piperidine hydrochloride prepared from piperidine itself and then purified by two precipitations by ether from its alcoholic solution.

The dry residue was purified in the same way, and then compared with pure piperidine hydrochloride. The appearance of the crystals was the same in the two cases (see Figure 2), the percentage of ionized chlorine also was the same

Pure product Extracted product

FIG. 2.—Crystals of piperidine hydrochloride magnified 12 times. In each case the characteristically shaped ends of the crystals are evident.

(29.1 and 29.1 per cent), and their melting points were 243° C and 242° C, respectively (242° C for a mixture of the two)[10]. This was sufficient to establish the identity of piperidine hydrochloride as the secondary compound. Furthermore, modified chlorinated rubber contains practically no nitrogen; traces of nitrogen which may be found by analysis are eliminated by extraction with alcohol.

Thermoplasticity.—Measurements of the Shore hardness as a function of temperature of heating were made with moulded discs. The results are shown in Figure 3. It was found that 20 per cent of piperidine renders chlorinated rubber slightly thermohardening, for, above 165° C, the hardness remains constant, whereas it decreases progressively as a function of the temperature, in the case of chlorinated rubber which has not been treated with piperidine.

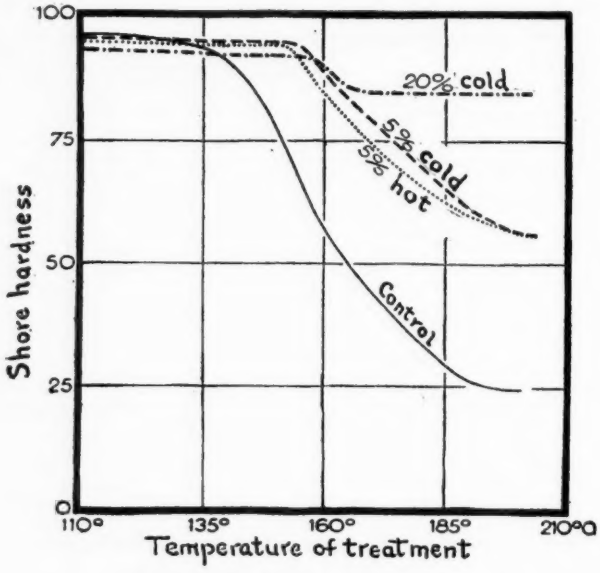

FIG. 3.—Thermoplasticity of chlorinated rubber before and after treatment with 5 and 20 per cent of piperidine.

Expansion by heating.—The diameters of the moulded discs were measured while the temperature was raised 10° C every 30 minutes. The results are shown in Figure 4.

Solubility.—When the amount of piperidine which is made to react with chlorinated rubber does not exceed 5 per cent, the products obtained are soluble in solvents of ordinary chlorinated rubber; however, the solutions obtained are brown and more viscous. Chlorinated rubber which has been modified by higher percentages of piperidine swells more or less, and dissolves only partially. This solubility is diminished still further by heating the modified chlorinated rubber, as may be seen in Figure 5. Modified chlorinated rubber prepared from 20 per cent of piperidine can be separated, by the action of benzene, into a soluble part and an insoluble part. The insoluble part, which is more important, since it represents 70 per cent of the product, is composed of hard, brown particles, which are more thermoplastic and contain a lower percentage of com-

bined chlorine than the soluble phase, which is obtained in the form of a very friable powder of ochre color. These two phases are, therefore, distinctly different.

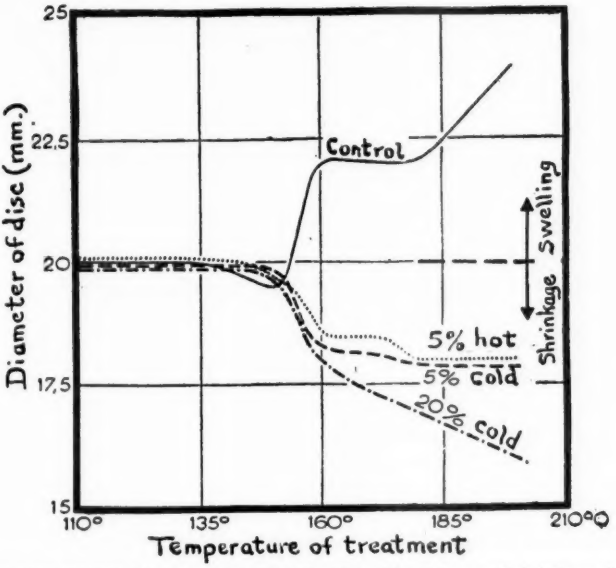

FIG. 4.—Swelling brought about by heating chlorinated rubber alone, and shrinkage of products treated with 5 and 20 per cent of piperidine.

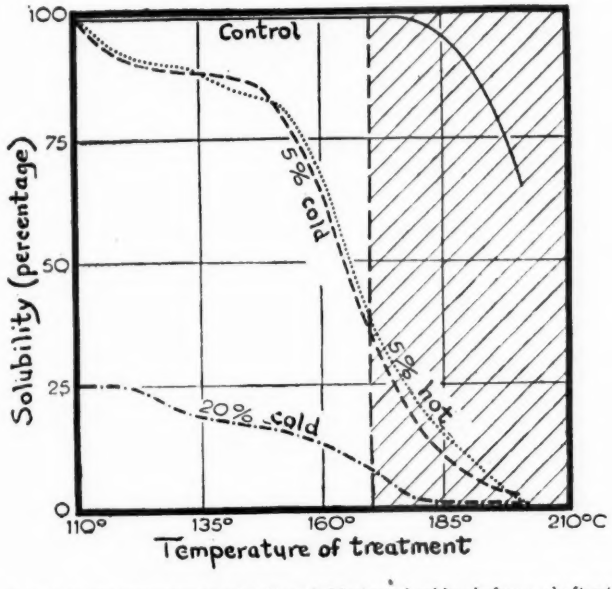

FIG. 5.—Effect of heat on the reduction in solubility of chlorinated rubber before and after treatment with piperidine. The cross-hatched section represents the region in which decomposition commences.

Iodine number.—The iodine number, which is zero for ordinary chlorinated rubber, is a very low but positive value, *viz.*, 2.3, for modified chlorinated rubber prepared with 5 per cent of piperidine. Because of their insolubility it was not possible to determine the iodine numbers of products prepared with higher percentages of piperidine. However, the results which were obtained show that the reactions must take place without extensive formation of double bonds. This in turn lends support to the mechanism of the reaction described at the beginning of this paper.

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ROLE OF CARBON IN OXIDATION OF GR-S VULCANIZATES *

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Oxygen was shown to be a major factor in the deterioration of GR-S tread stocks[1], and a quantitative study of the rate of oxygen absorption by GR-S vulcanizates was described in the preceding paper of this series[2]. Since reinforcing carbons are essential in most GR-S stocks for developing adequate physical properties, it seemed desirable to study the role of carbon in the oxidation.

Little information is available with respect to the effect of carbon on the oxidation of natural rubber. Ruby and Depew[3] observed that a carbon black stock did not age so well as a tread stock loaded with zinc oxide. They state that, although the cause is uncertain, it appears that "carbon black acts as a catalyst and oxidizes the soft rubber to a hard rubber". Vogt[4] compared the rate of oxygen absorption with gain in weight for a tire stock with various pigments. He found that the "gas black" stock absorbed the most oxygen and gave the poorest aged properties, whereas "thermatomic carbon" was intermediate between it and the inert fillers.

EXPERIMENTAL PROCEDURE

The volumetric method of measuring oxygen absorption, in which the sample is held at constant temperature and oxygen pressure, was used throughout this study. The absorption is reported in terms of the volume of oxygen (calculated to 25° C at 760 mm.) taken up by the sample during various time intervals. The apparatus and experimental details were described completely in a previous publication[2], in which it was shown that the actual reaction rate can be accurately determined by this method and that the effect of cure is negligible. The method is subject to less variation than aging studies based on physical property measurements, and the rate of oxidation is not masked by the effect of variations in compounding on changes in physical properties.

The following base formulation was employed:

	Parts by weight
GR-S	100.0
Bardol	5.0
Fat acid	1.5
Zinc oxide	5.0
Sulfur	2.0
Santocure	1.2
Carbon black	Variable

All stocks were cured for 50 minutes at a steam temperature of 298° F.

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* Reprinted from *Industrial and Engineering Chemistry*, Vol. 38, No. 10, pages 1052–1056, October 1946. This paper was presented before the Division of Rubber Chemistry at the 109th meeting of the American Chemical Society at Atlantic City, April 9–12, 1946.

The loadings employed with the various carbons studied are noted at the appropriate point in each of the following sections on the effect of loading, surface area, and surface activity.

EFFECT OF CHANNEL BLACK LOADING

To investigate the role of carbon black in the oxidation of GR-S, the rate of oxygen absorption at both 90° and 100° C was determined for stocks with various loadings of Spheron-9. The results are shown graphically in Figures 1 and 2, in which the volume of oxygen absorbed per gram of GR-S in the

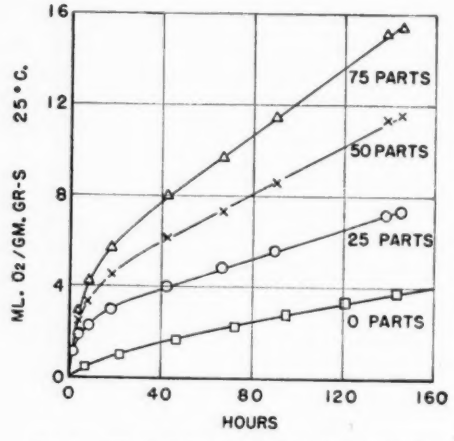

FIG. 1.—Effect of channel black loading at 90° C. 760 mm., cured 50 minutes at 298° F

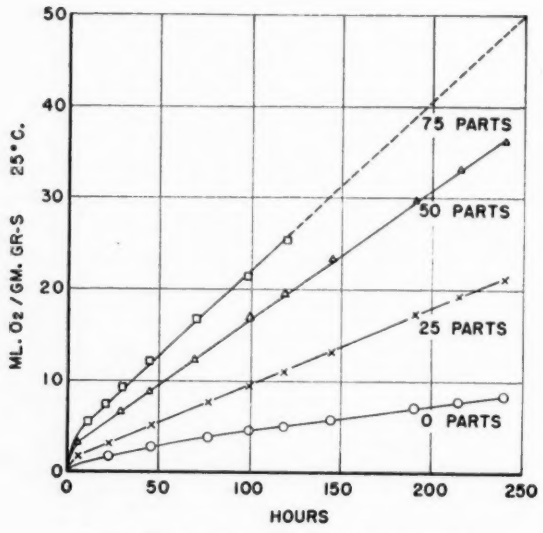

FIG. 2.—Effect of channel black loading at 100° C. 760 mm., cured 50 minutes at 298° F

sample is plotted against time in hours. It is clearly shown that the amount of oxygen absorbed during both the initial and linear portions of the curve is greatly dependent on the loading. Thus, although carbon black is essential for the reinforcement of GR-S, it is responsible for increasing the rate of oxidation. The type of black and the loading to be used in any given compound should, therefore, include consideration of both factors.

It was demonstrated previously[2] that the isothermal absorption of oxygen by GR-S vulcanizates follows the equation:

$$V = V_0(1 - e^{-k_1 t}) + k_2 t \qquad (1)$$

where V is the total volume absorbed at any time, t, V_0 is a constant for a given stock, and k_1 and k_2 are rate constants for pseudo first- and zero-order reactions, respectively. The temperature coefficients for k_1 and k_2 are 3.9 and 2.6, respectively, as reported in the previous paper for a stock with 50 parts of channel black. The energy of activation of the initially faster reaction (36,000 calories) is thus higher than that of the slower reaction (26,000 calories). This must indicate that the factor S in the Arrhenius equation $k = Se^{-E/RT}$ must be larger for the fast reaction than for the slow one. A higher value of S for the fast reaction indicates essentially that the entropy of activation for the formation of the transition complex has a more positive value than it has for the slow reaction. These rate constants were evaluated from the data of Figures 1 and 2 at both 90° and 100° C for channel black loadings ranging from 0 to 75 parts per 100 parts of GR-S. The values are presented in Table I together with the observed V_0 values.

TABLE I

RATE CONSTANTS AT VARIOUS CHANNEL BLACK LOADINGS

Parts loading/100 parts GR-S	V_0		k_1		k_2	
	90° C	100° C	90° C	100° C	90° C	100° C
0	1.80	1.8	0.018	0.04	0.015	0.029
25	2.68	1.2	0.164	..	0.032	0.084
50	3.75	2.4	0.157	0.61	0.055	0.144
75	4.80	3.6	0.160	..	0.075	0.188

In the derivation of the absorption equation it was postulated that the initial rapid absorption of oxygen was caused by reaction with a limited number of highly reactive centers in the vulcanizate, and that V_0 represents the volume of oxygen required to react completely with these centers. V_0 should, therefore, be constant for any given stock and should be independent of temperature. This is true for the unloaded stock. When carbon is present, however, the reaction of 100° C becomes so rapid that it is difficult to obtain the initial volume reading at true zero time and, consequently, the observed V_0 is smaller than the corresponding value at 90° C, The V_0 values increase by a constant amount for each 25-part increment of loading at both 90° and 100° C. The rate constant k_1 is independent of carbon loading at 90° C providing some carbon is present, but it is much smaller in the complete absence of carbon. By analogy the same behavior would be expected at 100° C. The absolute value of k_1 was more difficult to establish at the higher temperature because of the rapid rate of reaction. However, the value reported for the 50-part loading may be considered reliable because it represents the result of a number of separate determinations. The k_1 values for the 25- and 75-part carbon loadings were

omitted from the table because of the uncertainty in the observed values based on single determinations. However, they were of the same order of magnitude as that reported for the 50-part loading.

The constancy of k_1 and the dependence of V_0 on loading suggest that potentially active centers must be brought within the catalytic influence of the channel black before they become reactive, and, with increased loading, a larger proportion of these centers become activated. Therefore, k_1 for the stocks containing carbon is the rate constant for the reaction of oxygen with a limited number of potentially active centers which have been activated by the channel black. That there are a limited number of these active groups present in the gum stock is shown by the value of V_0 at 90° and 100° C. However, these centers—not activated by any carbon—react much more slowly.

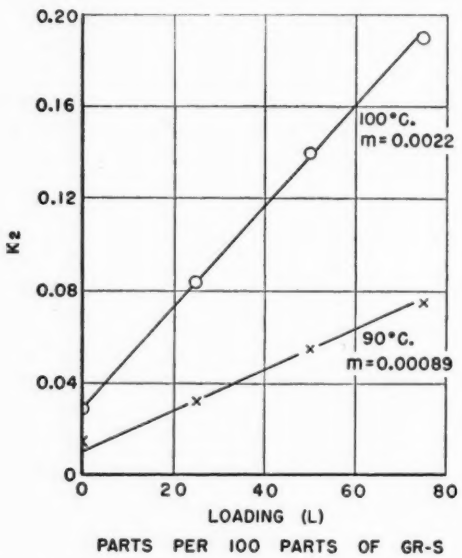

FIG. 3.—Effect of channel black loading on rate constant k_2.

It was further postulated that the slower linear rate of absorption represents the combination of oxygen with other oxidizable centers and proceeds from the start of the test. The rate constant k_2 for this reaction increases linearly with carbon loading at both 90° and 100° C (Figure 3). The intercept (k_0) at each temperature is, therefore, the rate constant for the reaction of oxygen with GR-S in the absence of channel black.

With increased loading of carbon, a greater proportion of oxidizable centers in the polymer fall within the catalytic influence of the black; consequently, since the rate of the catalyzed reaction is greater, the total rate is increased correspondingly. Thus, k_2 actually is a combination of two rate constants: k_0 for the reaction with centers not catalyzed by carbon, and k_L for the reaction with similar centers under the catalytic influence of the channel black. This relation is shown by the equation:

$$k_2 = k_0 + k_L L \qquad (2)$$

where L = carbon loading, grams per 100 grams GR-S
k_0 = intercept when $L = 0$
k_L = rate of the catalyzed reaction per gram of black
k_2 = observed linear rate of absorption

This equation expresses the relation in Figure 3, in which k_0 is the intercept and k_L is the slope m. Values of k_2 calculated from Equation 2 are compared with the observed values in Table II.

TABLE II

CALCULATED AND OBSERVED VALUES OF k_2

Channel black loading	90° C		100° C	
	Calculated	Observed	Calculated	Observed
0	0.010	0.015	0.029	0.029
25	0.032	0.032	0.084	0.084
50	0.054	0.055	0.14	0.14
75	0.077	0.075	0.19	0.19

Inserting the new constants for k_2 in Equation 1 yields Equation 3:

$$V = V_0(1 - e^{-k_1 t}) + (k_0 + k_L L)t \qquad (3)$$

Values of V_0 and k_1 are shown in Table I, and the values of k_0 and k_L are:

Temperature (° C)	k_0	k_L
90	0.010	0.00089
100	0.029	0.0022

The temperature coefficients for k_0 and k_L are 2.9 and 2.5, respectively, for the 90° to 100° C change in temperature. This represents an energy of activation of 28,600 calories for the reaction in the absence of carbon, and of 24,300 calories when under the catalytic influence of the channel black. The effect of the channel black is, therefore, to reduce the activation energy required for this reaction. Channel black may also function by absorption to produce a higher local concentration of oxygen, activated centers, or both. In any event the carbon is definitely functioning as a catalyst.

The loading constant k_L applies only to stocks containing the channel black used in this study, which was Spheron-9. Any change in either the nature or area of the carbon surface requires a new evaluation of this constant, as shown in the following section.

EFFECT OF CARBON SURFACE AREA

The increased rate of oxygen absorption with higher loadings of channel black (Figures 1 and 2) raises a question as to whether the observed effect was caused by the increase in amount of carbon present or merely results from the increased amount of carbon surface. Four channel blacks of a similar nature covering the 10- to 16-acre region and two furnace carbons in the 4- to 8-acre region were obtained for use in this and the following study. Three of the channel-type carbons were employed with the following loadings to give equal surface areas of carbon per gram of GR-S in each compound:

Channel black	Weight loading Parts/100, Parts GR-S	Surface area (Acres per lb.)
Micronex W6	52	10
Micronex Mark II	43	12
No. 242	33	15.7

The rate of oxygen absorption calculated per gram of GR-S associated with 45.0 square meters of carbon surface is plotted in Figure 4. The data for the two extremes, Micronex W6 and No. 242, are represented by a single curve. The small deviation of the curve for Micronex Mark II may be attributed either to experimental error or to a possible small error in the surface area value supplied to us by the manufacturer. In any event it is apparent that the rate of oxygen absorption depends on the surface area rather than on the weight of the carbon in the stock. Therefore, the k_L value determined for one channel black of known surface area may be modified so as to make it applicable to any channel black by multiplying it by the appropriate ratio of surface areas. The linear portion of the absorption equation then becomes:

$$k_2 t = [k_0 + k_L L(A_x/A)t] \tag{4}$$

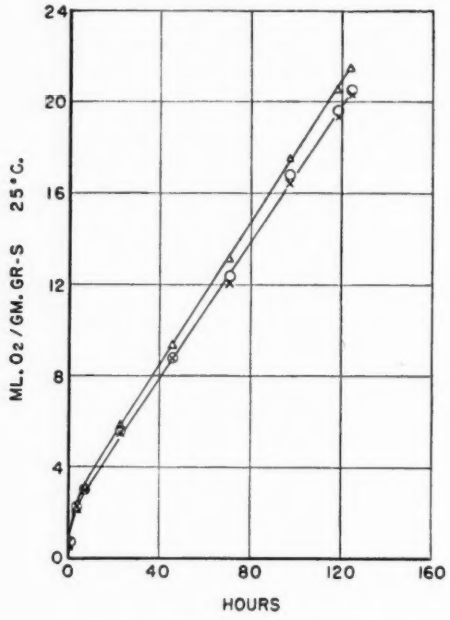

FIG. 4.—Effect of channel black surface area.
45.0 square meters per gram of GR-S, 100° C, 760 mm., cured 50 minutes at 298° F

○ Micronex W6	52 parts
△ Micronex Mark II	43 parts
× No. 242	33 parts

where A is the surface area per unit weight of the reference carbon used in evaluating k_L, and A_x is the corresponding surface area for any other channel black.

To test this theory the rate constant:

$$k_2 = k_0 + k_L L A_x/A \tag{5}$$

was calculated (using the value of k_L obtained with Spheron-9) for the three channel blacks employed in this study. The results are compared with the experimentally measured values in Table III; the agreement justifies this modification of the equation.

TABLE III

EVALUATION OF k_2 FOR DIFFERENT CHANNEL BLACKS

Black	Surface area A	Weight loading L	k_2 at 100° C	
			Calculated	Observed
Spheron-9	10	50	0.14	0.14
Micronex W6	10	52	0.14	0.15
Micronex Mark II	12	43	0.14	0.15
No. 242	15.7	33	0.14	0.16

It is of interest to note that a comparable relation between the specific surface of the carbon and certain physical properties of the vulcanizate has been reported in a recent paper by Parkinson[5].

EFFECT OF SURFACE ACTIVITY

Vulcanizates containing furnace blacks generally age better than similar ones containing channel black. This could result from differences in either the surface area or in the activity or nature of the respective surfaces. Therefore, three vulcanizates were studied, including one channel- and two furnace-type carbons, with appropriate loadings to give equal areas per gram of GR-S:

Black	Weight loading (parts per 100 parts GR-S)	Surface area (acres per lb.)
Standard Micronex	25.0	10.6
Statex B	33.1	8.0
Furnex	71.5	3.7

The rate of oxygen absorption per gram of GR-S associated with 23.7 square meters of carbon surface is shown in Figure 5. The curve for a gum stock compounded and vulcanized in the same fashion is included for comparison.

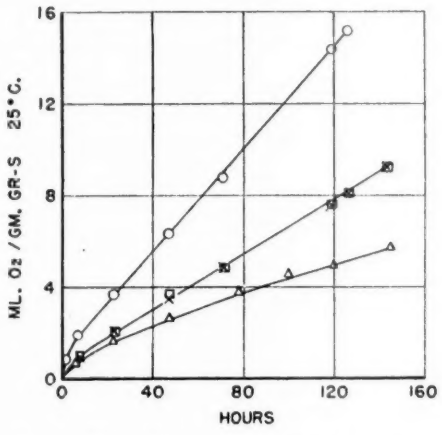

FIG. 5.—Effect of nature and area of carbon surface.
23.7 square meters per gram of GR-S, 100° C, 760 mm., cured 50 minutes at 298° F

○ Standard Micronex	25.0 parts
× Statex-B	33.1 parts
□ Furnex	71.5 parts
Δ Gum stock	

Since Furnex and Statex-B show the same rate of absorption per unit of surface area, the catalytic effect on the oxidation of GR-S is proportional to the carbon surface area for furnace carbons as well as for channel carbons. Although the Standard Micronex vulcanizate contained the same amount of

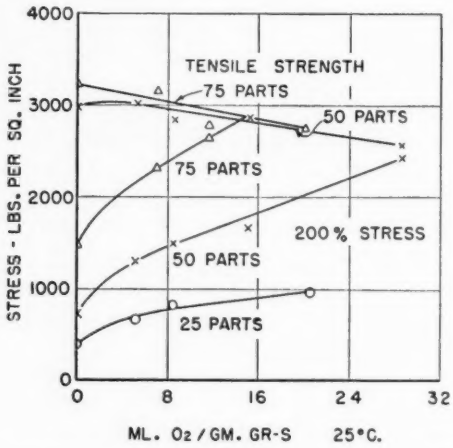

FIG. 6.—Effect of oxygen on physical properties at various channel black loadings. 100° C, 760 mm., cured 50 minutes at 298° F

carbon surface, the rate of oxygen absorption was much greater. Apparently the catalytic activity per unit of physical surface is greater for the channel black than for the furnace blacks. The relative surface activity for the two furnace carbons, based on the channel black taken as unity, is 0.55. It is therefore necessary to include a surface activity term, a, in the expression for k_2 in Equation 5:

$$k_2 = k_0 + ak_LL(A_x/A) \tag{6}$$

Using the value of k_L obtained with Spheron-9 and the appropriate surface areas and loadings of Standard Micronex and the two furnace carbons, the values of k_2 were calculated by Equation 6 and are compared with the experimental values in Table IV.

TABLE IV

EVALUATION OF k_2 FOR DIFFERENT TYPES OF CARBONS

	Relative activity a	Surface area A	Weight loading L	k_2 at 100° C	
				Calculated	Observed
Standard Micronex	1.0	10.6	25.0	0.09	0.11
Statex-B	0.55	8.0	33.1	0.061	0.061
Furnex	0.55	3.7	71.5	0.061	0.061

Substituting the expression for k_2 from Equation 6 in Equation 1 yields Equation 7:

$$V = V_0(1 - e^{-k_1t}) + [k_0 + ak_LL(A_x/A)t] \tag{7}$$

This equation is applicable to vulcanizates containing either channel or furnace blacks of different surface areas at any desired loading. The validity of this equation was established by the quantitative correlation of the rate of oxygen

absorption for stocks containing seven different carbon blacks, including both channel and furnace types, with surface areas ranging from 3.7 to 15.7 acres per pound, and with weight loadings ranging from 0 to 75 parts per 100 parts of GR-S. The close agreement between the calculated and observed values clearly indicates the validity of the assumptions on which the theoretical derivation was based.

The rate of oxygen absorption at other temperatures may be predicted by use of the constants and temperature coefficients reported in this and in the preceding paper[2].

CORRELATION WITH AGING

A question might be raised as to the extent to which the additional oxygen absorbed at higher loadings (Figure 2) is effective in producing changes in physical properties. The following program was carried out to determine the actual effect of a given amount of oxygen in degrading the properties of stocks having various carbon loadings.

Tensile strips from stocks with 25, 50, and 75 parts of channel black per 100 parts of GR-S were placed in the absorption tubes, and triplicate samples of each were removed for testing after appropriate time intervals. The times were 1, 2, and 4 days for the samples with 75 parts of black; 1, 2, 4, and 8 days for those with 50 parts; and 2, 4, and 8 days for those with only 25 parts. Tensile strength and stress at 200 per cent elongation are plotted in Figure 6 against the volume of oxygen absorbed per gram of GR-S in the sample.

The tensile curves for the 50- and 75-part loadings have similar rates of change per cc. of oxygen absorbed. If there is any real difference, it is in the direction of greater deterioration for a given amount of oxygen in the case of the higher loading. The tensile strength data for the aged samples with 25 parts of carbon were somewhat erratic and are not shown. However, the initial value of 1845 pounds per square inch and a final value of 1740 pounds per square inch after absorbing 20.6 cc. of oxygen indicate that the change produced by a given amount of oxygen was, if anything, less than that obtained with the higher loadings.

The stress at 200 per cent elongation increases at a greater rate for a given amount of oxygen as the loading is increased. This greater change with 75 parts of black took place in 4 days, whereas the smaller increase with the 25-part stock required 8 days. Thus the observed increase in the rate of oxygen absorption with higher carbon loadings is reflected in a rate of deterioration of physical properties which is at least correspondingly accelerated.

SUMMARY AND CONCLUSIONS

1. Carbon black is a catalyst for the oxidation of GR-S vulcanizates. The increased rate of oxygen absorption with increased loading is, however, a function of surface area rather than weight. Different types of carbons show different degrees of activity for a given surface area; the furnace carbons studied were, for example, only 55 per cent as active as channel black in promoting oxidation.

2. The rate constant for the initial rapid absorption of oxygen by GR-S tread stocks is independent of carbon loading. The presence of carbon is, however, essential to activate the centers involved in this initial stage, and the number of activated centers increases with carbon loadings, so that the amount of oxygen absorbed in a given time is also increased.

3. The second or linear stage of oxygen absorption involves two types of reaction with the remaining oxidizable centers in the polymer: a reaction with centers not under the catalytic influence of the carbon black, and a reaction catalyzed by carbon.

4. A theoretical equation was presented which permits the calculation of oxygen absorption by stocks containing either furnace- or channel-type carbons with various surface areas and loadings. The validity of the theory on which the derivation was based is supported by the quantitative correlation of calculated and observed rates of oxygen absorption for stocks containing carbons of both types, with surface areas ranging from 3.7 to 15.7 acres per pound and with loadings of 0 to 75 parts per 100 parts of GR-S.

5. The additional oxygen absorbed at higher loadings of carbon was shown to produce a correspondingly greater deterioration of physical properties.

ACKNOWLEDGMENT

The authors wish to express their appreciation to The Firestone Tire & Rubber Company for sponsoring this research and for permission to publish the results. They are particularly indebted to O. D. Cole of Firestone and C. F. Prutton of Case School of Applied Science for their continued interest and cooperation. Thanks are also due J. W. Snyder of Binney & Smith Company for supplying certain of the carbons required for this study.

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THE PERMEABILITY OF RUBBERLIKE SUBSTANCES TO GASES *

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INTRODUCTION

One of the important technical uses of rubber is made possible by the fact that its permeability to gases is very low. Various investigators[1] have been occupied with measurements of this permeability, and their studies have shown that, generally speaking, the passage of a gas through a rubber membrane involves several physical phenomena which are independent of one another. The gas first dissolves in the rubber to a degree which is proportional to the pressure, in accordance with Henry's law; it then diffuses in the rubber, in accordance with the law of Frick, toward that part of the rubber where the gas is present in a lower concentration; finally the gas evaporates out of the rubber.

The percentage of gas which passes through any membrane, under conditions of static permeability, can be expressed by the equation:

$$q = D \cdot h \cdot A \frac{p_1 - p_2}{d} \cdot t$$

where D is the diffusion coefficient, h is the solubility coefficient, A is the surface area of the membrane, p_1 and p_2 are the pressures on the two sides of the membrane, d is the thickness of the membrane, and t is the time.

By definition: $Q = Dh$, where Q is the permeability coefficient. This permeability coefficient is frequently confused with the diffusion coefficient.

If the diffusion coefficient D is expressed in cc. per second, and the solubility coefficient h, in accordance with Bunsen, by the number of cc. of gas at 0° C at 76 cm. pressure per cc. of rubber at a gas pressure of 1 atmosphere, then the permeability coefficient Q represents the number of cc. of gas at 0° C and at 76 mm. pressure that passes per second through a section of rubber having a surface of 1 sq. cm., a thickness of 1 cm., and difference in pressure of 1 atmosphere between the two sides of the membranes.

The factor D is L^2T^{-1} and the factor h if P^{-1}; hence Q is $L^2T^{-1}P^{-1}$ or $L^3M^{-1}T$.

It is evident then that, to evaluate in all its aspects the permeability of a material to any particular gas, it is necessary to determine separately the diffusion coefficient and the solubility coefficient[2]. However, as far as practical applications are concerned, only the permeability as such is of significance, and it was with a view first of all to obtaining technical data on this subject that the investigation described in the present paper was carried out.

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* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 21 No. 3, pages 50–56, March 1944. This paper is Communication No. 46 of the Rubber-Stichting, Delft, Holland.

EXPERIMENTAL METHOD

The present study had as its aim the determination of the permeability of a large number of vulcanizates. As a general rule, the measurements were limited to one gas, because it was assumed as a working hypothesis that when a given membrane shows poor permeability to a particular gas, it should show a correspondingly poor permeability to other gases. Account must, however, be taken of the fact that the permeabilities of different types of rubberlike materials differ to unequal degrees.

The gas with which measurements can be most conveniently made is hydrogen; furthermore data on the permeability of materials to this gas are of great importance, in the case for example, of balloons. This is the reason that permeability measurements published in the literature so frequently refer to hydrogen.

Taking advantage of earlier data[3], an apparatus has been developed with which it is possible to measure, by combustion, the permeation of hydrogen through any particular membrane to be studied. Figure 1 represents schematically the complete assembly, the operation of which is described below.

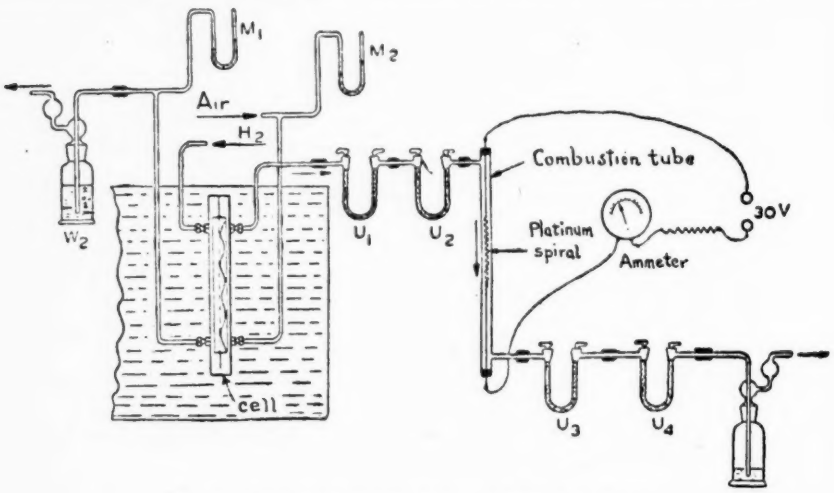

FIG. 1.—Apparatus for measuring permeability to hydrogen.

A gas cell[4], placed in a thermostat, is divided into two compartments of equal size by the rubber membrane to be tested. Hydrogen enters the left-hand compartment, then passes through a bubbler trap W_2, while dry air circulates in the right-hand compartment. This air, mixed with hydrogen which passes through the membrane, passes on first into the drying tubes, U_1 and U_2, which are filled, respectively, with blue silica gel, and pumice-phosphorus pentoxide. The gaseous mixture next passes into a combustion tube equipped with an incandescent platinum spiral, where the hydrogen burns to water. The water thus formed is collected in tubes U_3 and U_4. .The air is evacuated after having passed through the bubbler trap W_1 containing concentrated sulfuric acid. From the weights of the tubes U_3 and U_4 it is possible to calculate the permeability of the membrane to hydrogen.

The height of the liquid in W_1 and in W_2 is controlled in such a way that the

pressure in the hydrogen chamber is greater by 30 mm. than that prevailing in the other compartment. The air in the latter compartment is at the same pressure as the atmospheric pressure increased by 30 mm. of water. The pressures are read on the manometers, M_1 and M_2.

The cell, shown in Figure 2, is made up of two round steel plates, between which the rubber membrane to be tested is held. Vaseline is used to seal the joint between the membrane and the steel plates; this vaseline has a tendency to swell the rubber membrane slightly, but this has no harmful effect. To hold the membrane still better, the rings have very fine grooves.

So that the compartments can be swept out rapidly, they are as shallow as practicable. That for hydrogen has a depth of only 2 mm.; that for air a depth of 4 mm.; the latter carries a device for preventing the rubber membrane from being thrust back against the wall as a result of the excess pressure of the hydrogen. The diameter of the compartments is 15 cm.

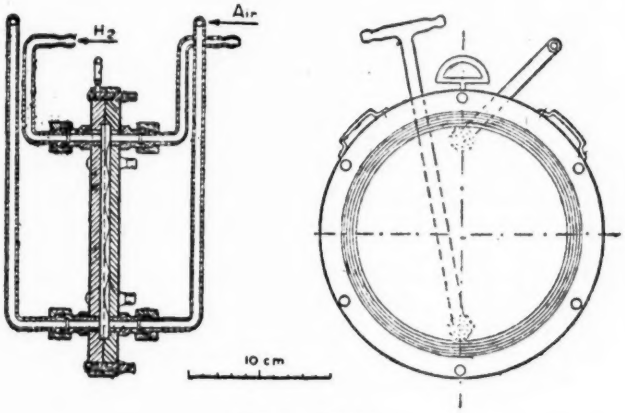

FIG. 2.—Gas cell.

The combustion tube, of Pyrex-Supermax glass, is 30 cm. long, and its internal diameter is 4 mm. The incandescent filament placed inside is a platinum wire 45 cm. long and 0.2 mm. in diameter, wound as a spiral for a length of 10 cm. It is brought to incandescence by means of a current of approximately 2.5 amperes and voltage of 30.

The operation is carried out in the following way. The cell, holding the rubber membrane, is placed in the thermostat and connected to the other parts of the assembly. Hydrogen and air are passed in for one hour before connecting the drying tubes, U_3 and U_4, into the circuit. The object of this preliminary operation is to expel air from the hydrogen chamber and to establish in the air chamber a uniform concentration of hydrogen. At the same time, the platinum spiral is brought to incandescence. The intensity of this incandescence is of no great importance, and as a general rule it is sufficient to hold it at a red heat.

The hydrogen and air circulate in the cell at a rate of 2 to 4 liters per hour. This rate is controlled in such a way that the concentration of air in the hydrogen compartment remain below 1 per cent so as to obtain perfect diffusion.

At the beginning of a measurement, the drying tubes, U_3 and U_4, are connected, and at the end of the operation they are disconnected from the assembly.

PREPARATION OF THE RUBBER MEMBRANES

The conditions which the membranes must fulfill in measuring their permeability are served. There must be no imperfections, such as pits or perforations, on their surface, which has a diameter of 18 cm., and the thickness must be as nearly uniform as possible. The most suitable thickness is 0.2 to 0.3 mm., which can be obtained technically without great difficulties.

Various methods may be used for preparing the rubber membranes.

(1) The unvulcanized mixture is carefully plasticized, and a portion is vulcanized under pressure between two aluminum plates in a hydraulic press. Above all else care should be taken to be sure that the surfaces of the plates are in perfect condition. Most of the membranes tested in the present investigation were prepared in this way.

(2) The unvulcanized mixture is calendered in such a way as to obtain membranes having the exact thickness and width desired. Various means can then be employed for vulcanizing the membranes, *e.g.*, under pressure between aluminum plates. Special attention should be paid to seeing that the air under the membrane has no possibility of escaping during vulcanization, otherwise fine holes in the membrane result. Compression between two sheets of tin gives the best results, for sheets of this metal can be removed without difficulty. This method of calendering is highly recommended for the preparation of membranes of stiff mixtures, *e.g.*, those having Buna-S or Perbunan as base. Particularly good membranes can be obtained from thermoplastic materials which do not need to be vulcanized, *e.g.*, Oppanol, Mipolam, and gutta-percha.

(3) Still another method is to prepare a solution and to apply it to a rubber support on cellophane[5], but such an apparatus is not in most cases available. Likewise it is possible to utilize, with satisfactory results, a glass plate on which is poured either the rubber in solution or in the form of latex; however, by this method only membranes of unloaded rubber can be prepared.

The mean thickness of a membrane is measured to 0.01 mm. by a Schopper comparator at 50 to 70 different points on the membrane. Any stray pits or perforations can be filled up with drops of latex.

MEASUREMENT OF THE PERMEABILITY COEFFICIENT FOR HYDROGEN OF MEMBRANES OF DIFFERENT COMPOSITIONS

Before commencing to make any actual measurements of membranes, a blank test of the apparatus should be made by passing air from both sides of the membrane under the normal conditions to be used in testing the membranes. The difference in weight of tubes U_3 and U_4 should not exceed 0.5 mg.

The time required to measure the permeability is about three hours. The values tabulated below, which are calculated from experimental measurements, represent the permeability coefficients as defined in the introduction of the present paper. As a general rule, these values have a precision of 1×10^{-8} for permeability coefficients higher than 20×10^{-8} and 0.5×10^{-8} for coefficients lower than 10×10^{-8}.

There will also be found at the end of the present paper data on the actual compositions of the membranes tested; in the present discussion only their most important characteristics will be mentioned briefly. All the data represent the means of four similar measurements, made with two different membranes at a constant temperature of $25° \pm 0.1°$ C.

ELASTOMERS OF DIFFERENT NATURES

The permeability coefficients of a series of elastomers as shown below were determined; for those which needed to be vulcanized, the compounding ingredients were kept low.

No.	Elastomer	Q value
1	Natural rubber	40×10^{-8}
2	Buna-S	30×10^{-8}
3	Buna-S degraded thermally	28×10^{-8}
4	Methyl rubber	13×10^{-8}
5	Perbunan	12.5×10^{-8}
6	Neoprene-G	11.5×10^{-8}
7	Neoprene-E	11.0×10^{-8}
8	Koroseal	8.0×10^{-8}
9	Oppanol B-200	5.5×10^{-8}
10	Mipolam-MP	4.5×10^{-8}
11	Thiokol-B	1.0×10^{-8}

The natural rubber mixture (No. 1), which will hereafter be called the base rubber mixture, showed the highest permeability.

It should be noted that the permeability is expressed in units by volume of the material in question. Since the service required of balloons requires membranes as light as possible, the specific gravity plays an important part in their composition. Neoprene has a specific gravity of 1.27, Thiokol-B 1.51; so from this point of view they are inferior to most other elastomers, the specific gravity of which range from 0.92 to 1.0. The value given for Perbunan agrees very well with the results obtained by Sager[6].

TESTS OF FILMS

The results of tests of various films show that Pliofilm (rubber hydrochloride) has a very low permeability; the process used in its manufacture has an influence on its permeability. The impression is gained, that, in this case, the permeability is due in part to very fine pores, for thick membranes showed permeability coefficients considerably higher than those of thin membranes.

No.	Elastomer	Thickness	Q
12	Pliofilm	0.035	1.1×10^{-8}
13	Pliofilm	0.045	1.8×10^{-8}
14	Pliofilm	0.06	3.0×10^{-8}
15	Triacel	0.06	4.0×10^{-8}
16	Cellophane	0.02	0.05×10^{-8}

By way of comparison, measurements were made of Triacel (triacetylcellulose) and Cellophane (cellulose). In agreement with the results of de Boer and Fast[7], these measurements show that Cellophane has a very low permeability, which in many cases could not be measured by the method used in the present work, and which must in some way be related to its large number of hydroxyl groups and resulting dense agglomeration of the molecules.

INFLUENCE OF THE PERCENTAGE OF COMBINED SULFUR

No.	Mixture	Q value	Combined sulfur
17	Rubber 100, sulfur 8, vulcanized 180 minutes	26×10^{-8}	4.9%
18	Rubber 100, sulfur 8, vulcanized 120 minutes	32×10^{-8}	3.2%
1	Base rubber mixture	40×10^{-8}	2.2%
19	Rubber mixture with thiuram	46×10^{-8}	0.4%

These measurements show clearly the great influence of the percentage of combined sulfur on the permeability to hydrogen, an effect which confirms the observations of Edwards and Pickering[8]. This decrease in permeability with increase in combined sulfur must be closely related to the increase in density of the rubber, which follows this increase in combined sulfur, as observed by McPherson[9].

INFLUENCE OF THE TIME OF VULCANIZATION

No.	Base rubber mixture	Q value	Combined sulfur
20	Unvulcanized	51×10^{-8}	0%
21	Vulcanized 10 minutes	42×10^{-8}	0.8%
1	Vulcanized 20 minutes	40×10^{-8}	2.2%
23	Vulcanized 80 minutes	38×10^{-8}	2.4%
22	Vulcanized 40 minutes	36×10^{-8}	3.0%

These results agree with those of the preceding paragraph, for the increase in the time of vulcanization is accompanied by a corresponding increase in the content of combined sulfur.

Figure 3 shows the relation between the permeability coefficient and the combined sulfur.

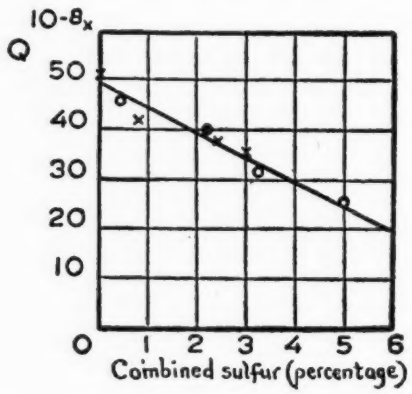

FIG. 3.—Relation between combined sulfur content and permeability.

COMPARISON OF DIFFERENT TYPES OF NATURAL RUBBER

No.	Base rubber mixture with	Q value
1	Ordinary crepe	40×10^{-8}
24	Deproteinized crepe	40×10^{-8}
25	Evaporated latex	39×10^{-8}

The three types of natural rubber which were tested are characterized by their differing contents of nonrubber components, notably proteins; however these substances apparently have hardly any influence on the permeability of the vulcanizates.

SOME UNVULCANIZED MATERIALS

No.	Material	Q value
20	Base rubber mixture, unvulcanized	51×10^{-8}
26	Evaporated latex, unvulcanized	39×10^{-8}
27	Gutta-percha, unvulcanized	16×10^{-8}

Contrary to what is true of the vulcanized rubbers, the nonrubber components of latex obviously have a great influence on the material before vulcanization. Gutta-percha, which is distinguished from rubber notably by its crystalline state, shows low permeability, a fact which is in accord with the increase in density which accompanies crystallization.

VULCANIZATES WITHOUT SULFUR

No.	Rubber vulcanized with	Q value
28	benzoyl peroxide	47×10^{-8}
29	*m*-dinitrobenzene	42×10^{-8}

The nature of the vulcanizing agent has little influence on the permeability.

PLASTICIZING AGENTS

No.	Base rubber mixture containing	Q value
1	No addition	40×10^{-8}
30	Stearic acid, 10 parts	37×10^{-8}
31	Coumarone resin, 10 parts	35×10^{-8}
32	Paraffin, 10 parts	36×10^{-8}
33	Carnauba wax, 10 parts	35×10^{-8}

The addition of a plasticizing agent has only a slight influence on the permeability.

FILLERS AND OTHER CHARGES

No.	Base rubber mixture with	Q value
1	No addition	40×10^{-8}
34	Barium sulfate, 20% by volume	33×10^{-8}
35	Channel carbon black, 20% by volume	29×10^{-8}
36	Silica, 20% by volume	29×10^{-8}
37	Chlorinated rubber, 50 parts	31×10^{-8}
38	Pliofilm, 50 parts	35×10^{-8}
39	Pliolite, 90 parts	19×10^{-8}
40	Plioform, 50 parts	34×10^{-8}
41	Polyethylene, 50 parts	24×10^{-8}
42	Acronal (a polyacrylic ester), 50 parts	25×10^{-8}

DIFFERENT ELASTOMERS

No.	Composition	Q value
1	Base rubber mixture	40×10^{-8}
43	Rubber, 100 parts + Perbunan, 100 parts	27×10^{-8}
5	Perbunan	12.5×10^{-8}
44	Rubber, 100 parts + Oppanol B-200, 50 parts	25×10^{-8}
45	Rubber, 100 parts + Oppanol B-200, 100 parts	16×10^{-8}
9	Oppanol B-200	5.5×10^{-8}
46	Rubber, 100 parts + Thiokol-B, 100 parts	17×10^{-8}
11	Thiokol-B	1×10^{-8}
47	Rubber, 100 parts + Mipolam, 50 parts	33×10^{-8}
10	Mipolam	4.5×10^{-8}
48	Rubber, 100 parts + gutta-percha, 43 parts	38×10^{-8}
27	Gutta-percha	16×10^{-8}

The addition of inorganic fillers[10] to rubber increases the effective thickness of the membrane, for, whereas, a gas can follow a rectilinear path in rubber which contains no filler, it must follow a broken path through rubber which does contain a filler. Furthermore, the addition of a filler reduces the effective surface of the membrane. Both these two effects reduce the permeability,

and this reduction is proportionally greater than the percentage of filler added. This is particularly evident with carbon black and with silica, in which cases the permeability is reduced 38 per cent by a reduction in rubber content of only 16.5 per cent. With barium sulfate the permeability is reduced only 19 per cent. In this case it is probable that a third effect plays a part, *viz.*, the weak adhesion of this filler to rubber[11], whereby even a small tension forms vacuoles between the rubber and the particles of barium sulfate, and this increases the permeability.

Among the mixtures described above, that containing Pliolite (like Plioform a cyclized rubber) is noteworthy. The vulcanizate is only slightly elastic, but is very flexible. By the direct addition of chlorinated rubber, Pliofilm or Pliolite on the mill, poor mixes are obtained; these ingredients should instead be added in the form of solutions in organic solvents to the rubber on the mill, and the solvents allowed to evaporate.

It is evident that the permeability of a mixture of two elastomers is intermediate between the values for the two individual components of the mixture. Figures 4, 5 and 6 represent the binary systems: rubber-Perbunan, rubber-Oppanol, and rubber-Thiokol. Mixture no. 45, containing equal parts of

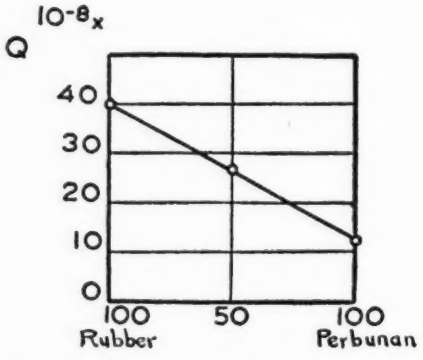

FIG. 4.—Coefficient of permeability of rubber-Perbunan mixtures to hydrogen.

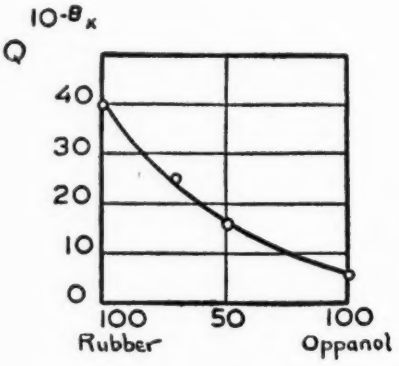

FIG. 5.—Coefficient of permeability of rubber-Oppanol mixtures to hydrogen.

rubber and Oppanol, deserves special attention, because its permeability is only slightly greater than that of Perbunan or of Neoprene when the permeability is expressed on a weight basis. It is 40 per cent of the permeability of natural rubber, while the permeability values of Neoprene and Perbunan are approximately 35 per cent of the permeability of natural rubber. It should be noted that the addition of Oppanol to rubber lowers disproportionately the permeability of the latter. From the point of view of permeability, Oppanol alone is an almost ideal material, but for technical use it has the disadvantage of low tensile strength, which is only 20 kg. per sq. cm., and an extensibility of 1,100 per cent. In this respect Oppanol can be improved by the addition of natural rubber and vulcanization.

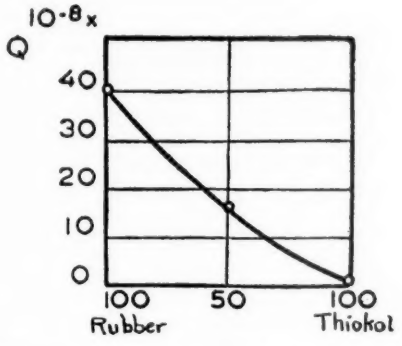

FIG. 6.—Coefficient of permeability of rubber-Thiokol mixtures to hydrogen.

The addition of gutta-percha to rubber reduces the permeability of the latter only slightly. This is quite understandable, for the addition of gutta-percha to rubber destroys the crystallinity of the latter, and it is this crystalline state which is the cause of the low permeability of rubber.

BENTONITE CLAY

When latex is mixed with a 5 per cent aqueous dispersion of bentonite (a colloidal clay), there is obtained, after evaporation, a rubber with considerably modified properties[12], particularly in its much greater stiffness. After incorporating vulcanizing ingredients, calendering, and vulcanizing, the product has a Q value which shows that bentonite lowers the permeability to an extraordinary degree.

By way of comparison, a mixture prepared in the conventional way with ordinary clay was studied. A great difference between the results obtained with ordinary clay and with bentonite was found.

No.	Mixture	Q value	Density	$Q \times$ density
1	Base rubber mixture	40×10^{-8}	0.97	39×10^{-8}
49	Latex + 10% bentonite	23×10^{-8}	1.11	26×10^{-8}
50	Latex + 15% bentonite	12.5×10^{-8}	1.17	14.5×10^{-8}
51	Latex + 20% bentonite	11×10^{-8}	1.33	14.5×10^{-8}
52	Latex + 30% bentonite	9.5×10^{-8}	1.47	14×10^{-8}
53	Latex + 40% bentonite	11.5×10^{-8}	1.23	14×10^{-8}
54	Rubber + 20% ordinary clay	24×10^{-8}	—	—

Figure 7 shows the permeability as a function of the content of bentonite. After a rapid lowering to a point corresponding to 15–20 per cent by volume of bentonite, the decrease in permeability is very small.

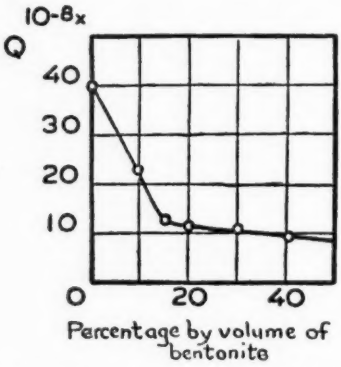

FIG. 7.—Effect of bentonite on the coefficient of permeability to hydrogen.

From the viewpoint of the technical use of such a mixture, there are two reasons for not exceeding a bentonite content of 15–20 per cent by volume. In the first place, when calculated on a weight basis, the permeability is not reduced when a volume of bentonite of 15–20 per cent is exceeded, as is shown by the values in the last column of the table above, in which the products of the permeability and density are listed. It should again be mentioned in this connection that density plays an important part in the manufacture of balloons. In the second place, the tensile strength decreases with increase in the content of bentonite, as is evident from the following data.

No.	Composition	Minutes of vulcanization	Tensile strength (kg. per sq. cm.)	Elongation at break (percentage)
50	Latex + 15% bentonite	20	185	425
52	Latex + 30% bentonite	30	115	300
53	Latex + 40% bentonite	40	95	225

OPPANOL AND BENTONITE

According to Table 1, the addition of a combination of Oppanol and bentonite to rubber results in a still greater lowering of the permeability. The best results were obtained with 10 or 20 per cent by volume of bentonite.

DISCUSSION

To prepare, with natural rubber as a base, a vulcanized product having low permeability to hydrogen, it is recommended that one of the following three combinations be used:

(1) a mixture of equal parts of rubber and Oppanol;
(2) rubber containing 15–20 per cent by volume of bentonite, prepared by starting with a mixture of latex and bentonite;
(3) a combination of mixtures (1) and (2).

For the manufacture of balloon fabrics, the latex-bentonite mixture can be applied on the fabric.

No.	Mixture		Q value	Specific gravity (d)	Q. d	Cure (min. at 147°)	Tensile strength (lbs. per sq. in.)	Elongation (percentage)
45	Rubber	100	16×10^{-8}	0.95	15×10^{-8}	40	152	1130
	Oppanol	100						
55	Latex*	100	10.0×10^{-8}	1.02	10×10^{-8}	50	125	725
	Oppanol	100						
	Bentonite	10						
56	Latex	100	8.0×10^{-8}	1.10	9×10^{-8}	60	97	625
	Oppanol	100						
	Bentonite	20						
57	Latex	100	8.5×10^{-8}	1.17	10×10^{-8}	60	64	425
	Oppanol	100						
	Bentonite	30						

* In the latex mixtures, the percentages are expressed as volumes and are based on the rubber contained in the latex.

MEASUREMENTS OF STRETCHED RUBBER

When rubber is stretched to 250–300 per cent elongation, x-ray examination shows the appearance of crystallization phenomena. It is generally assumed that the rubber molecules, which have no ordered state when the rubber is not stretched, are oriented as a result of the stretching, and become arranged parallel to one another so that crystallization is possible. Crystallization in turn increases the density of the rubber, and accordingly it would be expected that, as is the case with gutta-percha, stretched rubber would have a lower permeability.

In view of this, it seemed important to make some measurements of stretched rubber.

Since a stretched membrane of rubber is very susceptible to tearing, the edges of the two parts of the cell were covered with rubber in such a way that the membrane was pressed between two layers of rubber. The membrane was stretched by hand by two persons. Tests were carried out on vulcanized membranes which were stretched in one direction and also in all directions. Since it was not possible to prepare membranes in sections greater than 25–30 cm. while the apparatus had a section of 20 cm., it was not possible to elongate membranes strictly in only one direction. If a membrane is stretched in one direction to four times its original length, the width and thickness become half their original dimensions, and the membrane is then too thin. In most cases the rubber samples were stretched in one direction at the expense of their thickness.

The surface area of the stretched membrane was measured with a planimeter, and from this area and the original thickness, it was possible to calculate the thickness of the membrane while stretched. The elongations lengthwise and transversely were determined approximately. The following results were obtained. The vulcanizate was the so-called base rubber mixture (No. 1).

These tests were carried out at 25° C, and the values represent the means of several measurements.

As was to be expected, the permeability was lower when the rubber was stretched in one direction to 350–400 per cent elongation. In test no. 5, the rubber was stretched considerably in all directions, but it was found that stretch-

Test	Extension: Direction	Extension: Percentage	Thickness when stretched (mm.)	Q value
1	surface	150	0.12	37×10^{-8}
2	surface	240		
	lengthwise	250		
	transverse	−25	0.095	40×10^{-8}
3	surface	380		
	lengthwise	150		
	transverse	100	0.065	42×10^{-8}
4	surface	390		
	lengthwise	390		
	transverse	0	0.048	32×10^{-8}
5	surface	740		
	lengthwise	250		
	transverse	150	0.026	29×10^{-8}
6	surface	435		
	lengthwise	400		
	transverse	0	0.058	25×10^{-8}
7	surface	510		
	lengthwise	460		
	transverse	10	0.049	24×10^{-8}
8	surface	410		
	lengthwise	400		
	transverse	0	0.058	27×10^{-8}

ing in only one direction gave the best results, as shown by tests no. 3 and no. 4, in which the surface elongation was practically the same, membrane no. 3 being stretched in all directions, membrane no. 4 only in one direction.

It was found impracticable to test membranes at higher elongations, for the tension was then so high that there was great danger of tearing.

MEASUREMENT OF THE PERMEABILITY TO CARBON DIOXIDE

The same apparatus used for the measurements with hydrogen can be used, with certain modifications, for measuring permeability to carbon dioxide.

Carbon dioxide is led in through the same inlet tube used for hydrogen (see Figure 1), and that part of the carbon dioxide which passes through the membrane is carried away by a current of air. After having been dried, this air passes through a series of absorption tubes containing soda-lime and a product for absorbing the carbon dioxide. From the increase in weight of these tubes it is possible to calculate directly the permeability to carbon dioxide. The other conditions are the same as those used in measuring the permeability to hydrogen.

The following values, which are correct to within 1×10^{-8} to 5×10^{-8}, represent the means of four measurements made on two membranes.

No.	Material	Q value
1	Natural rubber	110×10^{-8}
2	Buna-S	93×10^{-8}
5	Perbunan	28×10^{-8}
6	Neoprene-G	22×10^{-8}
4	Methyl rubber	7×10^{-8}
9	Oppanol B-200	6×10^{-8}
11	Thiokol-B	3×10^{-8}

According to these results, permeability to carbon dioxide is in a general way greater than permeability to hydrogen. This can probably be attributed to the fact[13] that carbon dioxide is approximately fifteen times more soluble than hydrogen; hence, in spite of the much lower rate of diffusion of carbon dioxide through the various elastomers, it passes through them more rapidly than does hydrogen.

COMPOSITIONS OF THE MEMBRANES TESTED

No. 1 Crepe rubber 100, sulfur 3, diphenylguanidine 1, zinc oxide 3; vulcanized 20 min. at 147° C.

No. 2 Buna-S 100, sulfur 1.5, Vulkacit-ZA 1.8, phenyl-β-naphthylamine 1, zinc oxide 5, stearic acid 2; vulcanized 30 min. at 142° C.

No. 3 Buna-S (degraded thermally) 100, other ingredients those in No. 2; vulcanized 30 min. at 142° C.

No. 4 Methyl rubber (I.G.) 100, other ingredients those in No. 2; vulcanized 45 min. at 142° C.

No. 5 Perbunan 100, other ingredients those in No. 2; vulcanized 30 min. at 142° C.

No. 6 Neoprene-G; vulcanized 15 min. at 142° C.

No. 7 Neoprene-E; vulcanized 50 min. at 142° C.

No. 8 Koroseal.

No. 9 Oppanol B-200 (polyisobutylene).

No. 10 Mipolam-MP, with plasticizing agent.

No. 11 Thiokol-B 100, stearic acid 1, zinc oxide 10; vulcanized 25 min. at 142° C.

No. 17 Crepe rubber 100, sulfur 8; vulcanized 180 min. at 147° C.

No. 18 Crepe rubber 100, sulfur 8; vulcanized 120 min. at 147° C.

No. 19 Crepe rubber 100, thiuram accelerator 3, stearic acid 1, zinc oxide 5; vulcanized 30 min. at 135° C.

No. 20 Mixture No. 1; not vulcanized.

No. 21 Mixture No. 1; vulcanized 10 min. at 147° C.

No. 22 Mixture No. 1; vulcanized 40 min. at 147° C.

No. 23 Mixture No. 1; vulcanized 80 min. at 147° C.

No. 24 Deproteinized crepe rubber 100, other ingredients as in No. 1; vulcanized 20 min. at 147° C.

No. 25 Evaporated latex 100, other ingredients as in No. 1; vulcanized 17 min. at 147° C.

No. 26 Evaporated latex; unvulcanized.

No. 27 Gutta-percha, purified.

No. 28 Crepe rubber 90, benzoyl peroxide 10; vulcanized 10 min. at 147° C.

No. 29 Crepe rubber 100, *m*-dinitrobenzene, litharge 10, vulcanized 30 min. at 147° C.

No. 30 Mixture No. 1 100, stearic acid 10; vulcanized 20 min. at 147° C.

No. 31 Mixture No. 1 100, coumarone resin 10; vulcanized 20 min. at 147° C.

No. 32 Mixture No. 1 100, paraffin 10; vulcanized 20 min. at 147° C.

No. 33 Mixture No. 1 100, carnauba wax 10; vulcanized 20 min. at 147° C.

No. 34 Mixture No. 1 100, barium sulfate 95.6 (20 per cent by vol.); vulcanized 20 min. at 147° C.

No. 35 Mixture No. 1 100, channel carbon black 39.2 (20 per cent by vol.); vulcanized 25 min. at 147° C.

No. 36 Mixture No. 1 100, silica 50 (20 per cent by vol.); vulcanized 25 min. at 147° C.

No. 37 Crepe rubber 100, chlorinated rubber (Tegofan-4) 50, sulfur 2, Vulkacit-P 1, stearic acid 1, zinc oxide 5; vulcanized 45 min. at 110° C. (The chlorinated rubber was added in the form of a benzene solution.)

No. 38 Crepe rubber 100, Pliofilm 50, sulfur 2, Vulkacit-P 1, stearic acid 1, zinc oxide 5, magnesium oxide 5; vulcanized 45 min. at 110° C.

No. 39 Crepe rubber 100, Pliolite 90, other ingredients as in No. 37; vulcanized 45 min. at 110° C. The Pliolite was added in the form of a benzene solution.

No. 40 Crepe rubber 100, Pliolite 50, other ingredients as in No. 37; vulcanized 45 min. at 110° C.

No. 41 Mixture No. 1 100, polyethylene 50; vulcanized 25 min. at 147° C.

No. 42 Mixture No. 1 100, Acronal 50; vulcanized 25 min. at 147° C.

No. 43 Crepe rubber 100, Perbunan 100, sulfur 3, Vulkacit-AZ 3, phenyl-β-naphthylamine 2, stearic acid 3, zinc oxide 10; vulcanized 30 min. at 142° C.

No. 44 Crepe rubber 100, Oppanol B-100 50, sulfur 3, mercaptobenzothiazole 1, stearic acid 1, zinc oxide 3; vulcanized 30 min. at 147° C.

No. 45 Crepe rubber 100, Oppanol B-200 50, other ingredients as in No. 44; vulcanized 40 min. at 147° C.

No. 46 Crepe rubber 100, Thiokol-B 100, sulfur 3, mercaptobenzothiazole 1, stearic acid 0, zinc oxide 10; vulcanized 20 min. at 147° C.

No. 47 Mixture No. 1 100, Mipolan-MP (containing plasticizing agent) 50; vulcanized 25 min. at 147° C.

No. 48 Crepe rubber 100, purified gutta-percha 30, sulfur 3, diphenylguanidine 1, zinc oxide 3; vulcanized 25 min. at 147° C.

No. 49 Evaporated-latex rubber 100, bentonite 28 (10 per cent by vol.), sulfur 3, mercaptobenzothiazole 3, stearic acid 1, zinc oxide 3; vulcanized 40 min. at 147° C.

No. 50 Evaporated-latex rubber 100, bentonite 4 (15 per cent by vol.), other ingredients as in No. 49; vulcanized 30 min. at 147° C.

No. 51 Evaporated-latex rubber 100, bentonite 56 (20 per cent by vol.), other ingredients as in No. 49; vulcanized 40 min. at 147° C.

No. 52 Evaporated-latex rubber 100, bentonite 84 (30 per cent by vol.), other ingredients as in No. 49; vulcanized 40 min. at 147° C.

No. 53 Evaporated-latex rubber 100, bentonite 112 (40 per cent by vol.), other ingredients as in No. 49; vulcanized 40 min. at 147° C.

No. 54 Mixture No. 1 100, Devolite clay 58 (20 per cent by vol.); vulcanized 25 min. at 147° C.

No. 55 Mixture No. 49 100, Oppanol B-200 100; vulcanized 40 min. at 147° C.

No. 56 Mixture No. 51 100, Oppanol B-200 100; vulcanized 40 min. at 147° C.

No. 57 Mixture No. 52 100, Oppanol B-200 100; vulcanized 30 min. at 147° C.

CONCLUSIONS

The measurements of the permeability of various elastomers to hydrogen which have been described make particularly evident the following points.

The permeability values of Perbunan, Neoprene and Oppanol are from one-third to one-eighth those of natural rubber.

The higher the percentage of combined sulfur in natural rubber, the lower the permeability.

The addition of a plasticizing agent has only a small effect on the permeability.

The addition of progressively greater percentages of inorganic or organic fillers brings about a disproportionately great reduction in permeability.

Among mixtures of natural rubber with other compounding ingredients, three mixtures in particular are noteworthy for their low permeability:

(1) A mixture of equal parts of natural rubber and Oppanol (polyisobutylene).
(2) A mixture of rubber with 15–20 per cent by vol. of bentonite, prepared by starting with latex.
(3) A combination of these two types of mixtures (1) and (2).

Finally it was proved experimentally that stretched rubber has a lower permeability than the corresponding unstretched rubber, probably as a result of crystallization of the stretched rubber.

ACKNOWLEDGMENT

The author wishes to express his thanks to the Dutch Rubber Foundation for allowing the publication of this work, to Professor A. van Rossem for his encouragement and helpful advice, and to Professor C. Zwikker for his aid in writing the thesis submitted at Delft in 1943, of which the present work constitutes a part.

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THE PERMEABILITY OF DIFFERENT RUBBERS TO GASES AND ITS RELATION TO DIFFUSIVITY AND SOLUBILITY *

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INTRODUCTION

As far back as 1831 Mitchell[1] discovered that a rubber membrane is permeable to gases and that the rate of permeation differs with different gases. With the advance of synthetic rubbers in recent years it furthermore became evident that there is a marked difference in the behavior of these various types of rubber in the presence of a given gas. While this divergence in the behavior of different gases and kinds of rubber is primarily of great technical importance, *e.g.*, for balloons and inner tubes, it also offers interesting aspects from the theoretical point of view.

All the experimental data[2] show that, with rubber, the process of permeation is one of solution of the gas molecules on one side of the membrane, followed by diffusion through the rubber to the other side where the gas evaporates. Another fact which has been brought out is that the quantity of dissolved gas in the rubber is proportional to the pressure, following Henry's law, while Fick's law applies to the actual process of diffusion. On this assumption, the quantity of permeating gas q is determined by[3]:

$$q = DhA[(p_1 - p_2)/d]t \tag{1}$$

where

D = the diffusivity
h = the solubility
A = the area of the membrane
d = the thickness of the membrane
p_1 and p_2 = the pressures on both sides of the membrane
t = the time

If unit values are taken for the difference in pressure $p_1 - p_2$, the area A, the thickness d, and the time t, then:

$$Q = Dh \tag{2}$$

where Q stands for the permeability.

The units which will be used can be seen from this formula. According to Bunsen, the solubility h is expressed by the number of cc. of gas of 0° C and 76 cm. Hg which dissolves per cc. of rubber and 1 atm. gas pressure. The diffusivity D is expressed in sq. cm. per second and the permeability Q by the number of cc. of gas at 0° C and 76 cm. Hg which penetrates 1 sq. cm. of the surface of a piece of material 1 cm. thick per second when the outside difference

* Reprinted from the *Journal of Applied Physics*, Vol. 17, No. 11, pages 972–985, November 1946. This is Communication No. 55 of the Rubber Foundation (Rubber-Stichting), Delft, Holland.

in pressure of the gas amounts to 1 atmosphere. The dimensions of Q are:

$$[l^2t^{-1}p^{-1}] \quad \text{or} \quad [l^3m^{-1}t]$$

The formulas above apply only if the rates of solution and evaporation are very great compared to the rate of diffusion; in other words, if the concentration of the gas in the rubber interface remains constant and equal to the concentration of equilibrium (according to Henry's law), irrespective of the rate of diffusion. For instance, permeation is a more complicated phenomenon with metals, where the rate of solution or evaporation of the gas often governs the rate of permeation. This is evident chiefly by the fact that the rate of permeation is no longer in inverse ratio to the thickness of the membrane. It has been experimentally proved, however, that formula (1) holds good for rubber, so with that material there is no reason to assume that the rate of solution has much influence on the rate of permeation.

Our purpose was to find out why a given kind of rubber possesses a distinctive permeability. To do this it is not sufficient to make permeability measurements alone; it is necessary to measure separately the factors, solubility and rate of diffusion of the gas in the elastomer, which together, determine the permeability. It is best, moreover, to determine the dependence of these two factors on the temperature, since the heat of solution and the activation energy of the diffusion can then be calculated, by which means better insight into the whole process can be obtained.

METHOD FOR THE DETERMINATION OF THE PERMEABILITY

The apparatus by the aid of which the permeability and rate of diffusion were measured works on the same principles as that designed by de Boer and Fast[4] and by Barrer[5], the characteristic feature of which is a permeability cell with a pressure gauge, as represented in Figure 1

A gas cell is made up of two parts of steel, A and B, containing gas chambers separated from each other by a rubber membrane. The gas is introduced into the chamber A, the volume of which is approximately 75 cc., while the chamber B, which is connected to a pressure gauge, is exhausted to approximately 0.1 mm. Hg pressure. To prevent the membrane from sagging, it is supported on fine gauze netting which, in turn, rests on a perforated iron table.

The flanges, when warmed, were given a thin coat of an asphaltic bitumen mixture so that, once they had been screwed down, the apparatus was completely gas-tight.

A McLeod pressure gauge, with a range up to 2.5 mm. Hg pressure and recording with an accuracy of 0.005 mm. Hg pressure, was used to measure the pressure in the vacuum chamber. By noting for some time the increase in pressure in the vacuum chamber due to the permeability of the rubber, the permeability Q can be found with the aid of the equation:

$$Q = \frac{dp}{dt} \times \frac{V}{p} \times \frac{d}{A} \times \frac{273}{T} \tag{3}$$

where

dp = increase in the pressure in B in time dt
p = gas pressure in the gas chamber A
V = volume of the apparatus on the vacuum side
d = thickness of the membrane
A = area of the membrane
T = average temperature of the vacuum chamber

The surface area A of the membrane was always 30.2 sq. cm. The thickness of the membrane was determined with a Schopper thixometer to within an accuracy of 0.005 to 0.01 mm. The gas pressure p, which should be constant during a test, was usually 760 mm. Hg. So that the measurements could be made at constant temperature, the gas cell was placed in a water thermostat. The membranes were made as described on a former occasion[6].

This apparatus has much to recommend it for permeability determinations, which can often be carried out very quickly and with considerable recording accuracy; the consumption of gas per determination is negligible. The determination of Q is accurate to within 5 per cent.

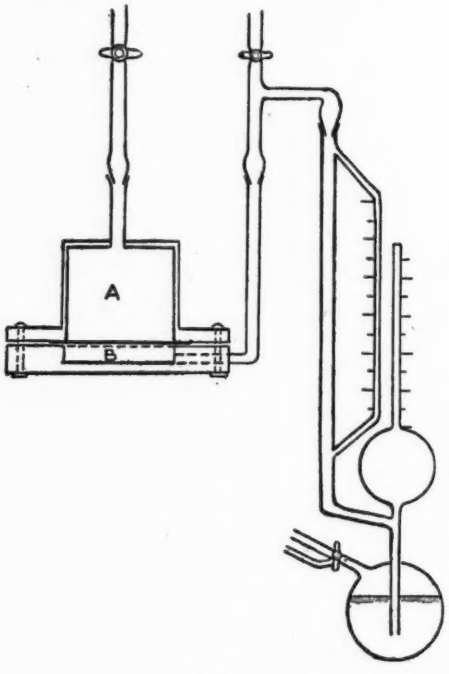

FIG. 1.—Apparatus for the measurement of the permeation and diffusion of gases in rubber.

METHOD FOR THE DETERMINATION OF THE RATE OF DIFFUSION

Using the foregoing permeability apparatus, the rate of diffusion can be measured, in combination with the permeability determinations, by a method evolved by Daynes[7] and Barrer[5]. If a gas is brought into contact with one side of a gas-free rubber membrane, it takes some time before the gas reaches the other side. This can be observed experimentally if the pressure of the vacuum (pressure gauge) side is plotted against the time, as in Figure 2.

It takes some time before there is constant increase in pressure, from which the permeability is computed. Daynes succeeded in finding an equation which correlates the time lag extrapolated to the zero axis θ, after which permeation begins, the diffusivity D and the thickness d of the membrane, starting from the diffusion equation:

$$\delta C/\delta t = D\delta^2 C/\delta x^2 \qquad (4)$$

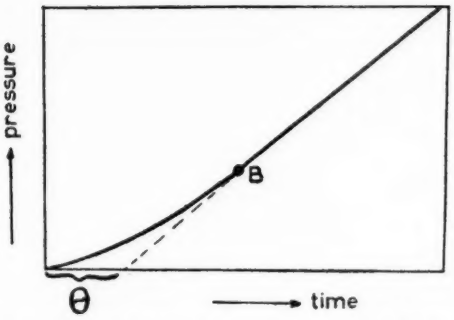

FIG. 2.—Relation between increase in pressure and the time.

The boundary conditions for the problem set are that:

1. for $x = 0$ and all t $C = C_0$
2. for $x = d$ and all t $C = 0$
3. for $t = 0$ and all x $C = 0$
4. A stationary condition prevails at $t = \infty$, so $\delta C/\delta t = 0$

From this an equation can be obtained which gives the concentration C of the gas in the membrane as a function of time t and place x:

$$C = C_0\left(1 - \frac{x}{d}\right) - \frac{2C_0}{\pi}\sum_{n=1}^{n=\infty}\frac{1}{n}\sin\frac{n\pi x}{d}\exp\left[-\left(\frac{n\pi}{d}\right)^2 Dt\right] \tag{5}$$

The amount of material which at the place $x = d$ in time t passes through the area A is:

$$q = AD\int_0^t -(dC/dx)_{x=d}dt \tag{6}$$

After determination of dC/dx from (5), substitution in (6) and integration, we get:

$$q = AD\left\{\frac{C_0 t}{d} - \frac{C_0 d}{6D}\sum_{n=1}^{n=\infty}1 - \exp\left[-\left(\frac{n\pi}{d}\right)^2 Dt\right]\right\} \tag{7}$$

To the stationary stage applies:

$$q = AD\frac{C_0 t_1}{d} \tag{8}$$

If $t = \theta + t_1$, then by combination of (7) and (8):

$$D = d^2/6\theta \tag{9}$$

Thus Equation (9) offers a simple means of calculating the diffusivity D from the thickness d of the membrane and the time lag θ of the permeability determination.

It is very important to know at what point the stationary condition begins. In this point (B of Figure 2) the term:

$$\sum_{n=1}^{n=\infty}\exp\left[-\left(\frac{n\pi}{d}\right)^2 Dt\right]$$

in Equation (7) approaches zero:

$$\sum_{n=1}^{n=\infty} \exp\left[-\left(\frac{n\pi}{d}\right)^2 Dt\right] = \sum_{n=1}^{n=\infty} \exp\left[-\frac{n^2\pi^2 t}{6\theta}\right]$$

because $D = d^2/6\theta$:

$$\sum_{n=1}^{n=\infty} \exp\left[-\frac{n^2\pi^2 t}{6\theta}\right] = \exp\left[-\frac{\pi^2 t}{6\theta}\right] + \exp\left[-\frac{4\pi^2 t}{6\theta}\right] + \exp\left[-\frac{9\pi^2 t}{6\theta}\right] + \cdots \quad (10)$$

If various values are put into (10) for t, it will be found that this term can practically be neglected after a time which is 2.5 to 3 times that of the time lag, and indeed it is usually from this point that extrapolation has taken place to the zero axis.

In using Equation (9) it has been assumed that the pressure in chamber B of Figure 1, which at most reached 2 to 3 mm. Hg, may be disregarded in comparison with the pressure in A, which usually amounted to 760 mm. Hg. The determination of D is accurate to 5–10 per cent.

The rate of diffusion through some materials is so slow that, as a result, the determinations sometimes take hours to carry out. For example, the time lag of the permeation of nitrogen through a membrane of Oppanol 0.20 mm. thick is 40 minutes at 17° C, so that 100 to 120 minutes elapse before the stationary condition sets in.

It need hardly be said that the membrane has to be degassed after each test by evacuation for a period which is 3 to 4 times the time lag.

An alternative to this method is to find the diffusivity as the quotient of the permeability and solubility, provided the solubility has been measured by some independent method, as described in the following section.

METHOD FOR THE DETERMINATION OF THE SOLUBILITY

It is possible to calculate indirectly the solubility of a gas in rubber from Equation (2), which shows it to be the ratio of the permeability Q to the diffusivity D.

This calculation requires, of course, the independent determination of Q and D without the use of Equation (2). A direct measurement of the solubility may be made with the apparatus shown in Figure 3.

A flask A, filled with fine snippings of rubber, is connected to a gas volume meter BC sealed with mercury. After chambers A and B have been exhausted, cock K is closed and chamber B filled with the gas under test. The gas is raised to exactly one atmosphere pressure by means of a movable mercury tube C. Cock K is then opened and the gas streams from chamber B to A. After waiting until equilibrium is attained, constantly adjusting tube C to maintain pressure at 1 atmosphere, the gas volume is read off. This volume of gas, less the nonrubber volume of flask A, gives us the quantity of gas absorbed by the rubber. Determination can be made at various temperatures by suspending A up to cock K in a water thermostat.

With most gases the test is accurate to 5 per cent. The solubility of carbon dioxide was determined to 1 to 2 per cent accuracy, as this was the most suitable of the gases for the apparatus.

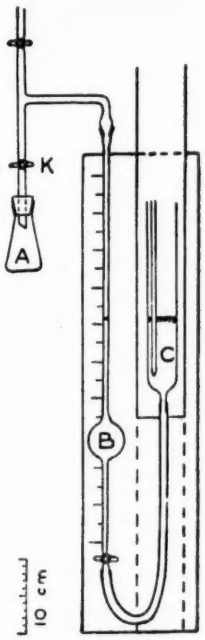

FIG. 3.—Equipment for measuring the solubility of gases in rubber.

EXPERIMENTAL TESTS

The rubbers used for the determinations were natural rubber, Buna-S, Perbunan, methyl rubber (polydimethylbutadiene) and butadiene rubber (polybutadiene) vulcanized for 30 minutes at 142° C in the proportions of 100 parts of rubber, 1.5 parts of sulfur, 5 parts of zinc oxide, 2 parts of stearic acid, 1.8 parts of Vulkacite-AZ, 1 part of phenyl-β-naphthylamine. Without any additions, Neoprene-G was vulcanized for 15 minutes at 142° C, while Thiokol-B was vulcanized with 10 parts of zinc oxide and 1 part of stearic acid for 25 minutes at 142° C. Thus any further mention of a particular kind of rubber always connotes a vulcanized one. This does not apply to Oppanol B-200 (polyisobutene) and Mipolam-MP (vinylchloridemethylacrylate copolymer), which cannot be vulcanized and therefore required no admixtures, though, as a commercial product, Mipolam-MP contains 27 per cent of softener.

The principal tests were preceded by a few hydrogen permeability determinations with natural rubber as a function of pressure and thickness to ascertain whether the quantity of permeating gas is proportional to the pressure and in inverse ratio to the thickness, as stated in the literature[8]. This proved to be correct, in measurements made between 160 and 1700 mm. Hg pressure with membranes of 0.20 to 1.01 mm. thick.

The results of the main work are recorded in Tables I and II.

The thickness of the membranes, which varied from approximately 0.2 to 1.1 mm, was always so chosen as to produce a measurable time lag. Of the gases used, hydrogen, oxygen, nitrogen, sulfur dioxide and ammonia were obtained from cylinders, the gas carbon dioxide being taken from a Kipp ap-

paratus. The methane was prepared by allowing water to drip into the Grignard compound of methyl iodide with magnesium.

To determine the solubility by the direct method it is necessary to know the specific gravity and the cubic expansion coefficient of the rubbers used. The

TABLE I

THE PERMEABILITY Q (IN 10^{-8} CM.^{2} SEC.$^{-1}$ ATMOS.$^{-1}$) AND THE DIFFUSIVITY D (IN 10^{-7} CM.^{2} SEC.$^{-1}$) OF GAS IN VARIOUS ELASTOMERS

	H_2			O_2			N_2			CO_2			CH_4		He
t in °C	Q	$D=\frac{d^2}{6\theta}$	$D=\frac{Q}{h}$	Q	$D=\frac{d^2}{6\theta}$	$D=\frac{Q}{h}$	Q	$D=\frac{d^2}{6\theta}$	$D=\frac{Q}{h}$	Q	$D=\frac{d^2}{6\theta}$	$D=\frac{Q}{h}$	Q	$D=\frac{Q}{h}$	Q
Natural rubber															
17°	28	79	76	12	12.5	12	4.1	8.0	8.3	72	6.7	7.1	12.5		16.5
25°	39	105	100	18	17.5	18	6.6	11.5	12.5	102	10.5	11	22	8.8	23
35°	58.5	140	140	28.5	27	28	11.0	20	21	145	17	18.5	36		33
43°	77	185	180	39	36	39	16	28	29	185	25	26	50	21	44
50°	97	220	230	49.5	49	49	22.5	37	40	220	32	34	64		
Buna-S															
17°	22.5	80		9.0	9.6		3.0	7.2		71	6.8		10.5		13
25°	30.5	100	85	13	14	14	4.8	10	10	94	10	11	16		17.5
35°	44	135		20	20		7.8	14.5		130	15.5		26		25
43°	59.5	165	150	27.5	28	30	11.5	21	23	165	23	24	35		33
50°	74	200		34.5	34		14.5	28		195	29		43		42
Perbunan															
17°	7.6	31		2.0	2.4		0.50	1.45		15	1.0		1.3		5.8
25°	11.5	42	41	3.2	3.6	4.0	0.89	2.3	2.5	23	1.7	1.8	2.4		8.7
35°	17.5	64		5.3	6.3		1.65	4.1		37	3.1		4.7		12.5
43°	25.5	86	82	7.7	9.1	9.6	2.5	6.2	6.3	52	4.7	5.3	7.0		16.5
50°	31.5	110		10.5	13		3.7	8.6		66	7.0		10.1		21
Neoprene-G															
17°	6.8	29		1.75	2.5		0.53	1.55		12.4	1.3		1.4		
25°	10.3	38	36	3.0	3.8	4.0	0.89	2.4	2.5	19.5	2.3	2.4	2.5		
35°	16	56		5.1	6.2		1.65	4.4		31	4.2		4.8		
43°	23	74	72	7.7	10.0	10.0	2.55	7.2	6.7	43.5	6.8	6.8	7.2		
50°	28.5	94		10.1	13		3.55	9.4		56.5	9.1		9.8		
Oppanol-B-200															
17°	3.0	10		0.54	0.50		0.11	0.27		2.3	0.32		0.2		3.8
25°	4.9	14	14	0.90	0.78	0.84	0.22	0.43	0.42	3.8	0.54	0.55	0.55		5.6
35°	8.3	21		1.6	1.55		0.44	0.84		6.6	1.05		1.1		8.5
43°	12	31	30	2.6	2.4	2.5	0.78	1.5	1.4	10.0	1.8	1.8	1.9		12
50°	16.5	38		3.7	3.4		1.15	2.1		14	2.5		2.9		15.5
Butadiene rubber															
17°	23	75		10.1	11		3.4	8.1		80	7.6				
25°	32	96		14.5	15		4.9	11		105	10.5				
35°	46	125		21	22		7.8	16		140	16				
43°	60	160		28	30		11	22		175	22				
50°	77	180		36	37		14.5	29		200	28				
Methyl rubber															
17°	9.0	27		0.93	0.88		0.20	0.46		3.0	0.36		—		8.1
25°	13	39		1.6	1.4		0.36	0.79		5.7	0.63		0.60		11
35°	20	61		3.1	2.5		0.78	1.7		10.5	1.3		1.45		16
43°	29	80		5.0	4.1		1.3	2.8		17	2.2		2.7		22
50°	38	105		7.1	6.1		2.2	4.1		24	3.6		4.4		27
Mipolam-MP															
17°	2.9	15		0.41	0.90					2.3	0.23				
25°	4.4	20		0.70	1.3		0.2			4.0	0.44				
35°	7.3	30		1.4	2.4		0.4			7.6	0.83				
43°	10.5	39		2.1	3.9		0.7			11.5	1.4				
50°	14	50		3.2	5.2					15	1.9				
Thiokol-B															
17°	0.71	7.8		0.11						1.3	0.43				
25°	1.2	10.5		0.22						2.4	0.81				
35°	2.2	18		0.49						4.8	1.7				
43°	3.3	26		0.85						7.7	2.8				
50°	4.6	35		1.3						11.0	4.0				

TABLE II

THE SOLUBILITY h OF GAS IN VARIOUS ELASTOMERS

	H_2		O_2		N_2		CO_2		CH_4	NH_3	SO_2
t in °C	Direct	$h=\frac{Q}{D}$	Direct	$h=\frac{Q}{D}$	Direct	$h=\frac{Q}{D}$	Direct	$h=\frac{Q}{D}$	Direct	Direct	Direct
Natural rubber											
17°	0.037	0.036	0.099	0.100	0.049	0.054	1.01	1.08	0.26		
25°	0.039	0.038	0.099	0.102	0.052	0.056	0.90	0.97	0.25	6.9	23.6
35°	0.041	0.040	0.100	0.104	0.053	0.058	0.78	0.83	0.25		
43°	0.042	0.042	0.100	0.105	0.055	0.059	0.70	0.74	0.24	4.1	11.6
50°	0.043	0.044	0.101	0.106	0.056	0.060	0.64	0.68	0.23		
Buna-S											
25°	0.036	0.031	0.093	0.094	0.048	0.048	0.87	0.92		8.1	17.2
43°	0.039	0.036	0.093	0.096	0.050	0.053	0.69	0.72		6.6	9.8
Perbunan											
25°	0.028	0.026	0.079	0.084	0.035	0.038	1.28	1.38		13.5	48.0
43°	0.031	0.029	0.080	0.084	0.040	0.041	0.98	1.08		8.0	23.5
Neoprene-G											
25°	0.029	0.026	0.075	0.075	0.036	0.036	0.83	0.83		8,8	18.1
43°	0.032	0.030	0.076	0.078	0.038	0.037	0.64	0.66		6.7	10.5
Oppanol B-200											
25°	0.035	0.034	0.107	0.110	0.052	0.049	0.69	0.69		1.25	3.6
43°	0.040	0.041	0.102	0.108	0.054	0.052	0.57	0.57		1.05	2.4
Butadiene rubber											
25°		0.034		0.094		0.045		0.97			
43°		0.039		0.097		0.049		0.82			
Methyl rubber											
25°		0.033		0.114		0.045		0.87			
43°		0.035		0.117		0.050		0.72			
Mipolam-MP											
25°		0.022		0.052				1.00			
43°		0.027		0.059				0.80			
Thiokol-B											
25°		0.011						0.30			
43°		0.013						0.28			

specific gravity was therefore determined at a number of different temperatures by the buoyancy method, *viz.*, by weighing on an analytical balance, the rubber, suspended on a hook, being dipped under water. The results are shown in Table III.

TABLE III

THE SPECIFIC GRAVITY AND THE CUBIC EXPANSION COEFFICIENT λ OF VARIOUS ELASTOMERS

	Sp. gr. at 15° C	λ between 15° and 40° C
Natural rubber (vulcanized)	0.9689	7.0×10^{-4}
Buna-S (vulcanized)	0.9974	6.7
Perbunan (vulcanized)	1.0316	6.2
Neoprene-G (vulcanized)	1.2470	6.2
Oppanol B-200	0.9306	6.2

The specific gravity is accurate to 0.001 and λ to 0.2×10^{-4}. Within the measured range the coefficient of expansion is not a function of the temperature.

The computed solubilities contain the error of the permeability and diffusion determinations. To reduce this error to a minimum, the solubility was not

calculated direct from the quotient of the permeability and diffusivity, but the latter quantities were first plotted logarithmically against $1/T$, as in Figures 4 and 5. From this the solubility was calculated graphically. This was a

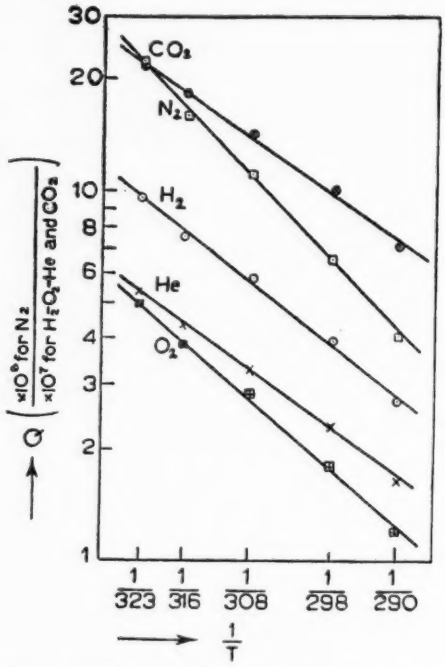

FIG. 4.—Relation between the permeability in natural rubber and temperature.

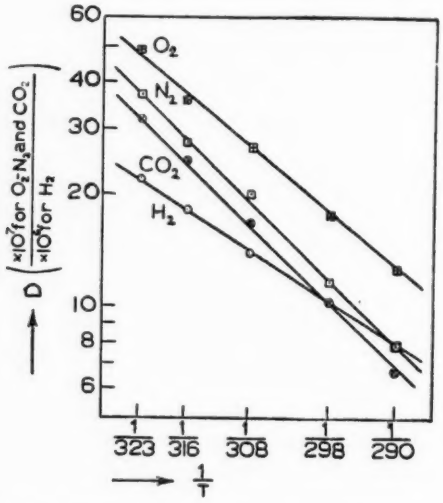

FIG. 5.—Relation between the diffusivity in natural rubber and temperature.

precautionary measure against two accidental errors producing a considerable error in the solubility. As these solubilities are accurate to 10 per cent, the results obtained by the direct method are the more reliable.

The permeabilities for hydrogen and carbon dioxide at 25° C agree within the experimental error with the permeabilities determined by other means in the presence of air[6]. It follows from this that it is immaterial whether there is a vacuum or some alien gas on the other side of the membrane, as was the case in the former experimental tests. Thus permeability to a given gas is not affected by the presence of an alien gas. There is, likewise, agreement between solubilities and diffusivities, which were determined in two ways in this work.

For practical purposes the permeabilities at 25° C of the various elastomers are calculated with reference to natural rubber in Table IV.

TABLE IV

THE PERMEABILITY OF ELASTOMERS AT 25° C WITH REFERENCE TO NATURAL RUBBER

	H_2	O_2	N_2	CO_2	CH_4	He
Natural rubber	100	100	100	100	100	100
Butadiene rubber	82	80	74	103	—	—
Buna-S	78	72	73	92	73	76
Methyl rubber	33	9	5.5	5.6	2.7	48
Perbunan	29	18	14	23	11	38
Neoprene-G	26	17	14	19	11	—
Oppanol B-200	12	5	3.3	3.7	2.5	24
Mipolam-MP	11	4	3	3.9	—	—
Thiokol-B	3	1.2	—	2.4	—	—

According to our results, the differences in permeability to a given gas are caused mainly by differences in rate of diffusion and only in a very minor degree by differences in solubility.

In Table V the permeabilities at 25° C have been referred to hydrogen. The differences in the permeability of a given elastomer to various gases are caused not only by great differences in rate of diffusion, but also to a consider-

TABLE V

THE PERMEABILITY OF ELASTOMERS AT 25° C WITH REFERENCE TO H_2

	H_2	O_2	N_2	CO_2	CH_4	He
Natural rubber	100	46	17	260	56	59
Butadiene rubber	100	45	15	330	—	—
Buna-S	100	43	16	310	52	57
Methyl rubber	100	12	2.8	44	4.6	85
Perbunan	100	28	7.7	200	21	76
Neoprene-G	100	29	8.6	190	24	—
Oppanol B-200	100	18	4.5	77	11	114
Mipolam-MP	100	16	4.5	91	—	—
Thiokol-B	100	18	—	200	—	—

able extent by differences in solubility. For example, the permeability to carbon dioxide is as a rule far greater than to hydrogen owing to the far greater solubility of carbon dioxide, which amply compensates for its far slower rate of diffusion.

CALCULATION OF THE ACTIVATION ENERGY OF THE PERMEATION, THE ACTIVATION ENERGY OF THE DIFFUSION AND THE HEAT OF SOLUTION

The thermal dependence of the permeability and the diffusivity takes an exponential course, as it appears that there is a linear relation between $\log Q$ or $\log D$ and $1/T$. Some of the results plotted in this way are shown in Figures 4 to 6, from which the applicability of the following formulas may be concluded:

$$Q = Q_0 e^{-W/RT} \tag{11}$$

and

$$D = D_0 e^{-E/RT} \tag{12}$$

where Q_0 and D_0 = constants, W = activation energy of the permeation, and E = activation energy of the diffusion.

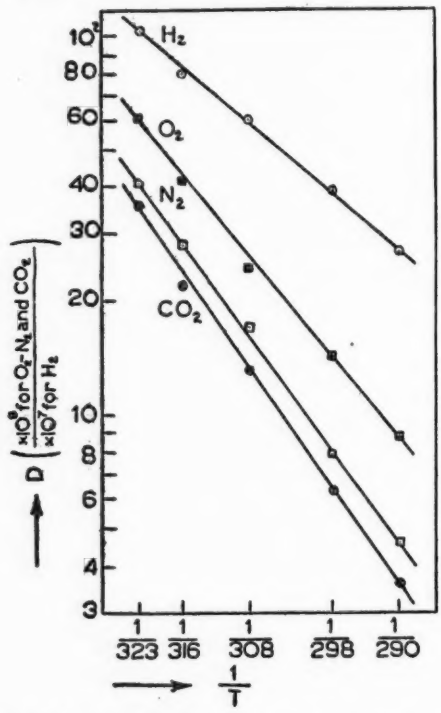

FIG. 6.—Relation between the diffusivity in methyl rubber and temperature.

The slope of the lines in Figures 4 to 6 gives a measure of the energy. The constants and the energies can be calculated with the aid of formulas (13) and (14), which follow from formula (12).

$$E = \frac{4.573 \log D_2/D_1}{1/T_1 - 1/T_2} \tag{13}$$

$$\log D_0 = \log D_1 + \frac{E}{4.573 T_1} \tag{14}$$

Dividing (11) by (12), we get:

$$\frac{Q}{D} = \frac{Q_0}{D_0} e^{(-W+E)/RT} \tag{15}$$

or

$$h = h_0 e^{(-W+E)/RT} \tag{16}$$

The solubilities which, in the case of natural rubber, were determined in complete thermal dependence, take an exponential course with the temperature.

The following formulas hold for the calculation of the heat of solution:

$$\frac{d \ln C_B/C_A}{dT} = \frac{H}{RT^2} \tag{17}$$

where H = heat of solution, C_B = concentration of the gas in the rubber, and C_A = concentration of the gas in the gas phase:

$$\frac{C_B}{C_A} = K_0 e^{-H/RT} \tag{18}$$

Therefore, to calculate this heat of solution, the proportion of the concentration of dissolved gas to the concentration of the gas in the gas phase must be known, *i.e.*, the number of cc. of gas of the prevailing temperature and pressure which is dissolved per cc. of solvent. It is quite simple to calculate this by multiplying our solubility figures, which are expressed in cc. of gas of 0° C and 76 cm., by $T/273$.

The calculation then becomes as follows:

$$\ln h \frac{T}{273} = -\frac{H}{RT} + \ln K_0 \tag{19}$$

$$\frac{d \ln h}{d1/T} = -\frac{H}{R} + T = -\frac{H'}{R} \tag{20}$$

$$H = RT + H' \tag{21}$$

Thus, to find the required heat of solution, one can multiply the solubility h by $T/273$ and plot the logarithm of this amount against $1/T$. Alternatively, the logarithm of the solubility h can simply be plotted against $0/T$ and RT cal. added to the "heat of solution" H' thus obtained.

RT cal. has likewise to be added to $W - E$ to calculate the heat of solution from the temperature function of the permeability and diffusivity.

The heat of solution obtained in this way represents the supply of heat necessary to dissolve 1 mole of gas in rubber saturated with gas.

Table VI shows the activation energy of the permeation W for the various processes of permeation with the conjoined constant Q_0. Measurements made by Barrer[5] and Sager[9] show satisfactory agreement with these figures. It is evident that both quantities have little intrinsic value. But the energy W was used for the calculation of the heat of solution, and it also permits of the calculation of the permeability Q for any desired temperature. Caution is, however, necessary when calculating the permeability in this way at temperatures well outside those of our measured range, as the energy W may be a function of the temperature; indeed, with methane, this already proved to be the case within that range, for which reason the activation energy W of methane was not calculated. At lower temperatures the increase in permeability with

TABLE VI

THE ACTIVATION ENERGIES W AND E WITH THE CONJOINED CONSTANTS Q_0 AND D_0 AND THE HEAT OF SOLUTION H IN CAL./MOLE

		Q_0	W	D_0	E	H
Natural rubber I (from Q and D determination)	H_2	0.046	6900	0.23	5900	1600
	O_2	0.080	6600	0.57	7500	800
	N_2	0.47	9300	2.9	8700	1200
	CO_2	0.036	6200	3.6	8900	−2100
	He	0.014	6500	—	—	—
Natural rubber II (from Q and h determination)	H_2	—	—	0.31	6100	1400
	O_2	—	—	0.66	7600	700
	N_2	—	—	2.8	8600	1300
	CO_2	—	—	3.3	8800	−2000
	CH_4	—	—	—	—	−1300
Buna-S	H_2	0.031	6800	0.056	5100	2300
	O_2	0.030	7300	0.23	7100	800
	N_2	0.12	8700	0.55	7800	1500
	CO_2	0.014	5700	0.90	8100	−1800
	He	0.013	6600	—	—	—
Perbunan	H_2	0.099	8100	0.96	7300	1400
	O_2	0.25	9400	2.6	9300	700
	N_2	1.1	11000	7.2	10200	1400
	CO_2	0.29	8300	12	10700	−1800
	He	0.012	7000	—	—	—
Neoprene-G	H_2	0.090	8100	0.28	6600	2100
	O_2	0.54	9900	3.1	9400	1100
	N_2	0.56	10600	9.3	10300	900
	CO_2	0.33	8500	20	10800	−1700
Oppanol B-200	H_2	0.47	9500	0.55	7600	2500
	O_2	0.66	10700	7.3	10800	500
	N_2	5.5	12800	18	11700	1700
	CO_2	0.98	10100	22	11700	−1000
	He	0.035	7900	—	—	—
Butadiene rubber	H_2	0.022	6600	0.053	5100	2100
	O_2	0.023	7100	0.15	6800	900
	N_2	0.053	8200	0.22	7200	1600
	CO_2	0.0069	5200	0.24	7300	−1500
Methyl rubber	H_2	0.10	8000	1.3	7500	1100
	O_2	3.3	11300	20	11100	800
	N_2	22	13300	105	12400	1500
	CO_2	9.7	11200	160	12800	−1000
	He	0.0078	6600	—	—	—
Mipolam-MP	H_2	0.15	8900	0.20	6800	2700
	O_2	3.2	11800	4.3	10200	2200
	CO_2	0.68	9800	27	12000	−1600
Thiokol-B	H_2	0.74	10600	2.0	8500	2700
	O_2	18	13500	—	—	—
	CO_2	6.0	11500	67	12100	

the temperature was greater than at higher temperatures. With carbon dioxide as well, a similar tendency to depart from the purely exponential course was observed within the measured range, but with this gas the discrepancies were usually too small to affect the calculation of the activation energy W.

Table VI also gives the activation energy of the diffusion and the heat of solution of gases in the elastomers under test. In the case of natural rubber, moreover, the heat of solution is calculated from the direct determination of the solubility. The activation energy of the diffusion followed from that heat of solution together with the activation energy of the permeation. The figures resulting from these two forms of calculation agree.

The determination of the activation energies of the permeation and of the diffusion is accurate to 200 cal. The reason why this is so much more accurate than measurement of the permeability and diffusivity alone is that the calculation of these energies does not necessitate the use of various particulars which themselves contain errors, like the thickness and area of the membrane and volume of the apparatus, since all that is needed to calculate W is to plot the logarithm of the pressure increase per unit of time (after conversion to 0° and 76 cm.) against $1/T$. It likewise suffices for the calculation of E to plot the logarithm of the time lag against $1/T$. In unfavorable cases, *i.e.*, when the errors in W and E reinforce each other, the determination of the heat of solution is faulty to 400 cal. The accuracy of Q_0 and D_0 is entirely governed by that of W and E. An error of 200 cal. in W or E makes Q_0 or D_0 faulty by approximately 30 per cent.

DISCUSSION OF THE SOLUBILITY

With the data we have collected, we shall now consider more closely the two factors which govern permeability, *viz.*, solubility and rate of diffusion, in an endeavor to find the reason for the magnitude of the permeability of rubber to gases. It will become apparent that the behavior of gases in rubber is entirely analogous to that of gases in organic liquids; hence rubber may be regarded as an organic liquid of very high molecular weight.

One of the striking facts which emerges from the solubility measurements is that the solubility of hydrogen and nitrogen in rubberlike substances increases as the temperature increases, from which it follows that heat must be supplied for the process of dissolving. This is contrary to Barrer's experience[5] on determining the solubility of hydrogen and nitrogen in some elastomers, when the solubility decreased as the temperature rose. Apart from the fact that we established the dependence of the solubility on the temperature in two unallied ways, our finding is the more probable because the solubility of these gases in organic liquids almost invariably increases together with the temperature[10]. More soluble gases, like carbon dioxide for example, always exhibit a decrease in solubility, on the contrary, in organic liquids as the temperature rises.

The explanation we suggest for this behavior of gases is the following[11].

The heat of solution H consists of a thermal value Q, depending on the chemical or physical action between gas and liquid molecules, and of a work A brought about by the passing of 1 mole of gas into the solution, hence:

$$H = A + Q \tag{22}$$

whereby the heat absorbed during solution and the work then exerted by the gas become positive factors in the calculation. Furthermore:

$$A = RT \ln P/p \tag{23}$$

A being regarded as the work produced on the conversion of 1 mole of gas from outside pressure P to the osmotic gas pressure p in the liquid. It should be noted that p/P is the solubility of the gas expressed as cc. of gas of the prevailing temperature dissolved per cc. of rubber.

If the concentration of the gas in the liquid is smaller than outside, A is positive. If Q is neglected, then $A = H$, with the result that the heat of solution H, which has to be supplied, is, likewise, positive, and solubility rises.

If, on the other hand, the concentration of the gas in the liquid is greater than outside, A is negative. Neglecting Q, it follows from this that the heat of solution H is negative and that the solubility decreases as the temperature rises.

Reference to Table VI will show that the heat of solution of a gas in elastomers is less positive or more negative in proportion to greater solubility. It has been found that the heat of solution of nitrogen and hydrogen in the various rubbers agrees fairly closely with the work of expansion as calculated from (23). The thermal value Q cannot be neglected in the case of the other gases. Taking carbon dioxide as an instance, its solubility is of a kind that the concentration of the gas inside and outside the rubber is about equal; hence the work A is very small, yet an appreciable negative value is found for the heat of solution.

The degree of solubility is governed by the nature of the gas and of the elastomer.

THE NATURE OF THE GAS

It is known that a gas with a high critical temperature or boiling point dissolves more readily in an organic liquid than a gas of lower critical temperature or boiling point[12]. The position of the critical temperature is a measure of the tendency of the gas to condense, with which the solubility stands in relation.

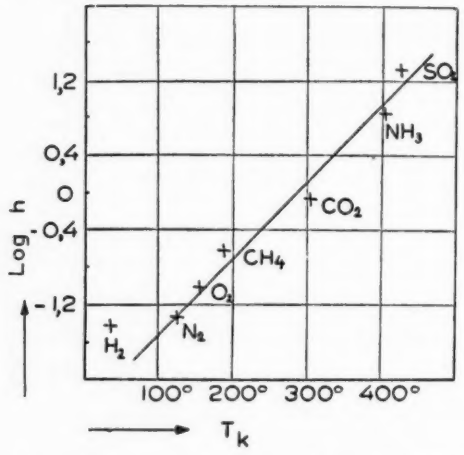

FIG. 7.—Relationship between the critical temperature and solubility of gases in natural rubber.

With rubbers, too, the solubility of the gas increases with the critical temperature[13]. As may be seen from Figure 7, a relation exists between the solubility h and the critical temperature of the gas T_k:

$$\log h = A + BT_k \qquad (24)$$

where A and B are constants.

H_2 is somewhat more soluble in rubber than would seem to follow from (24).

Körösy[14] found the same relation for the solubility of gas in organic liquids, with hydrogen showing a similar deviation.

THE NATURE OF THE ELASTOMER

The presence of polar groups reduces the solubility of a nonpolar gas in an organic liquid[15], for two electrically polar molecules have greater mutual attraction than two which are not polar. In a solution of nonpolar molecules in a polar solvent this greater mutual attraction more or less expels the nonpolar molecules. Contrarily, polar gas molecules dissolve more readily in a liquid with polar molecules than in a liquid without polar molecules.

All this is equally applicable to rubberlike substances. Perbunan with strong polar groups (−CN groups) has a reduced solvent power with respect to nonpolar gases—hydrogen, nitrogen and oxygen—and an increased solvent power on the polar gases sulfur dioxide and ammonia; on the other hand the saturated hydrocarbon Oppanol has very low solvent power for the polar gases. Perbunan also has an increased solvent power with respect to carbon dioxide, despite the fact that this gas has no dipole moment as have sulfur dioxide and ammonia. Nevertheless, carbon dioxide is not nonpolar, for it contains two polar groups, which neutralize each other exteriorly[16], one result of which is that, on the whole, carbon dioxide dissolves more satisfactorily in a substance with polar groups than in one without them, so in this case in Perbunan more than in natural rubber. The same thing is not found, however, with Neoprene (containing −Cl groups).

DISCUSSION OF THE ACTIVATION ENERGY OF DIFFUSION

The value of the diffusivity is governed by the value of the constant D_0 and the activation energy of the diffusion E. The activation energy E has to be supplied to separate the rubber chains—which are linked together by Van der Waals forces[17]—a sufficient distance to permit a gas molecule to be displaced or to make for itself a new place or hole. This energy is supplied by the kinetic energy of the gas molecule and particularly by the kinetic energy of the rubber molecules.

The degree of activation energy is governed by the nature of the gas and of the elastomer.

THE NATURE OF THE GAS

It might be expected that the larger the diameter of the gas molecule, the greater is the activation energy, since larger openings between the rubber molecules are needed for the diffusion of the larger gas molecules; consequently, these rubber molecules need to be separated over a greater length, for which more energy is required.

Figure 8 shows the activation energy in relation to the diameter d_T of the gas molecules used[18], which was determined from the internal friction. It appears that the activation energy of the diffusion approximately increases in proportion to the size of the gas molecules.

THE NATURE OF THE ELASTOMERS

It is to be expected that the stronger the secondary valencies by which the rubber molecules are interlinked, the greater is the activation energy of the diffusion E. These secondary valencies also govern the extent of the heat of evaporation and the cohesive energy of the molecules.

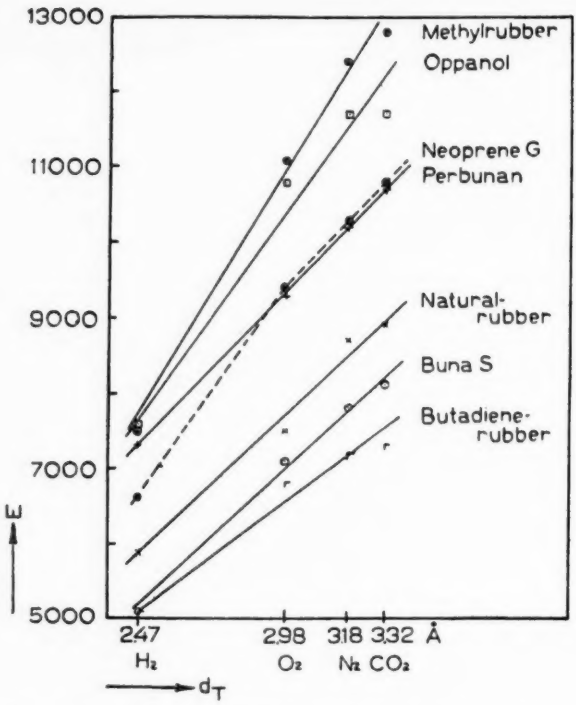

FIG. 8.—The activation energies of the diffusion in relation to the diameter of the gas molecules.

The introduction of methyl groups into rubber causes the cohesive energy to increase, as may be seen in Table VII, where each successive elastomer has one methyl group per structural unit more than the previous elastomer. It is evident that the activation energy and the cohesive energy are interrelated. This cohesive energy applies per unit of structure and is calculated by Dunkel's method[19]. We may conclude that approximately 1.5 to 2.5 units of structure have to be separated to allow the diffusion of one gas molecule.

TABLE VII

COMPARISON BETWEEN THE COHESIVE ENERGY AND THE ACTIVATION ENERGY E (IN CAL./MOLE)

	Cohesive energy	E_{H_2}	E_{O_2}	E_{N_2}	E_{CO_2}
Butadiene rubber	3960	5100	6800	7200	7300
Natural rubber	4370	5900	7500	8700	8900
Methyl rubber	4780	7500	11100	12400	12800

Oppanol is another instance of the considerable importance of the methyl groups in the molecule, for in it, as in methyl rubber, the activation energies for the diffusion were found to be very high. It is not possible in this case to calculate the cohesive energy following Dunkel, because the increment for this energy of a quaternary C atom is not known, but, compared with natural rubber, Oppanol may be expected to possess considerable cohesive energy per

linear unit of the chain molecule, as the Oppanol molecules contain a great many methyl groups.

The introduction of polar groups greatly increases the cohesive energy of molecules. Accordingly, a high activation energy of the diffusion is found in Neoprene and Perbunan as compared with butadiene rubber.

To sum up, for the investigated materials a considerable activation energy of the diffusion, and thereby a low rate of diffusion and low permeability, may be brought about by the presence in the elastomer of (1) polar groups, *e.g.*, Perbunan, Neoprene, Mipolam, and Thiokol; (2) methyl groups, *e.g.*, methyl rubber and Oppanol.

DISCUSSION OF THE CONSTANT D_0

Several attempts have been made in the literature[20] to relate the temperature function of the diffusivity to other quantities. Most of the formulas describing this relation are of the following type:

$$D = \tfrac{1}{6}\nu d^2 e^{-E/RT} \tag{25}$$

where ν is a frequency and d a length.

The factor $\frac{1}{6}\nu d^2$ then corresponds to the constant D_0 as determined by us. If the frequency ν is conceived as the number of vibrations executed by the gas molecule in the rubber and the length d as the free length of path of this gas molecule in the rubber, it would follow that D_0 must be roughly constant in the diffusion of a given gas in various rubbers. Actually there is great disparity between the D_0's. It was found, for example, that for N_2 $D_0 = 0.22$ to 105, depending very much on the activation energy E.

This makes it plain that a formula of this type does not hold good for rubber.

There is another formula, suggested by Barrer[21], which might meet the case, *viz.*:

$$D = \tfrac{1}{6}\nu d^2 \frac{(E/RT)^{f-1}}{(f-1)!} e^{-E/RT} \tag{26}$$

f = number of degrees of freedom.

This formula only applies if $(E/RT) \ll f - 1$.

If this formula is applied to our results, then E has been wrongly calculated, since the fact that D_0 may depend on the temperature has not been taken into account, for:

$$\frac{d \ln D}{d1/T} = -\frac{E}{R} + (f-1)T = \frac{-E(\text{determined})}{R} \tag{27}$$

Therefore, $(f-1)RT$ has to be added to the E already determined and this new E must be filled in (26). Barrer worked out the results of his diffusion measurements of gas in rubber with this formula and came to the conclusion that, to obtain a proper order of magnitude for D_0, the number of degrees of freedom must amount to 12 to 14.

We worked out some of our results with this formula, assuming that $\nu = 5 \times 10^{12}$ and that $d = 8$A. It makes no fundamental difference if some other amount is taken for these quantities.

It appears from Table VIII that the number of degrees of freedom may vary from 4 to 13, according to the activation energy, which does not clarify the problem at all. It is difficult to avoid the impression that f here is little more than a factor by which D_0 may be brought into the right order of magnitude.

TABLE VIII

CALCULATION OF THE NUMBER OF DEGREES OF FREEDOM f IN ACCORDANCE WITH FORMULA (26)

	D_0	E		Calculated
H_2—Buna-S	0.056	5100	$f = 4$	$D_0 = 0.051$
H_2—Natural rubber	0.23	5900	6	0.21
H_2—Perbunan	0.96	7300	8	0.93
N_2—Oppanol	18	11700	10	22
N_2—Methyl rubber	105	12400	13	96

So, as this course does not provide satisfactory information on the magnitude of D_0, we tried to draw up an experimental formula based on the great dependence of D_0 on E. For this purpose all the D_0 values found were logarithmically plotted against E (see Figure 9), with the result that a practically linear relation is found to exist between log D_0 and E. Barrer[22] also found this relation.

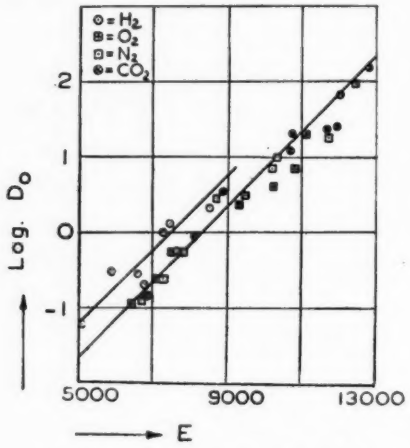

FIG. 9.—Relation between log D_0 and E.

The points in Figure 9 fall fairly clearly into two groups. The first group, with oxygen, nitrogen and carbon dioxide, follows by approximation a line which conforms to the equation:

$$\log D_0 = E/2000 - 4.2$$

or

$$D_0 = 6.3 \times 10^{-5} e^{E/870} \tag{28}$$

The second group with H_2 conforms by approximation to:

$$\log D_0 = E/2000 - 3.75$$

or

$$D_0 = 1.8 \times 10^{-4} e^{E/870} \tag{29}$$

It also follows from these formulas that hydrogen diffuses on an average about 2 to 3 times more quickly than oxygen, nitrogen and carbon dioxide, apparently on account of the greater average velocity of hydrogen molecules. The kind of rubber also seems to exert a specific influence, since gas diffuses in

natural rubber approximately twice as quickly and, in Oppanol and Mipolam, about twice as slowly as is to be inferred from the formulas. The combination of the formulas (28) and (29) with $D = D_0 e^{-E/RT}$ leads for nitrogen, oxygen and carbon dioxide to:

$$D = 6.3 \times 10^{-5} \exp\left[- E \left(\frac{1}{RT} - \frac{1}{870} \right] \right) \tag{30}$$

and for H_2 to

$$D = 1.8 \times 10^{-4} \exp\left[- E \left(\frac{1}{RT} - \frac{1}{870} \right) \right] \tag{31}$$

Hence these formulas apply by approximation to all species of rubber, the first one even to three gases. According to (30) and (31), the diffusivity D depends only, with a given gas, on E and the temperature; thus any random rubber could be roughly classified merely by measuring the rate of diffusion at a certain temperature. Indeed, with only one exception, the higher activation energies E were always found to go along with the lower diffusivity D.

There would be some justification for concluding from this reasoning that the considerable differences in the e-power are responsible for the great differences in the D_0's found and it may therefore be asked whether the differences in D_0 have any real significance.

The most serious problem with which one is faced when deriving a formula intended to meet all theoretical and experimental demands is that of accounting for the heat motion of the rubber molecules, and the failure of diffusion formulas which do satisfy other diffusion processes is probably caused by this inadequate allowance for the heat motion. This view accords with the results of an investigation carried out by Kuhn[23] into the rate of diffusion of organic dyes in swollen and deswollen rubber, where, likewise, the heat motion of the rubber molecules proved to be of decisive importance.

SUMMARY

Since the permeability of rubberlike substances to gases is related to the solubility and rate of diffusion of the gases in those materials, these individual values should be known. The permeability of a membrane was measured manometrically and the diffusivity was derived from the time lag of the permeation. The solubility of the gas was computed from the permeability and the diffusivity; the solubility was found by direct measurement. In this way eight different gases were tested with nine elastomers at different temperatures. The permeability of a membrane to a given gas is not affected by the presence of a second gas. The differences in permeability of different elastomers to a given gas are caused mainly by differences in rate of diffusion and only in a very minor degree to differences in solubility. Differences in permeability of the same elastomer to different gases are caused not only by differences in rate of diffusion but also by differences in solubility. A linear relationship was found between the logarithm of the solubilities of different gases in natural rubber and their critical temperatures, so the higher the critical temperature of a gas, the better it dissolves. The presence of polar groups in an elastomer reduces the solubility of nonpolar gases and increases the solubility of polar gases in the elastomer. The various rubbers behave towards gases like organic liquids. The activation energy of the diffusion and the heat of solution were calculated from the temperature function of the diffusivity and the solubility. As the

diameter of the molecule of the gas increases, the rate of diffusion decreases, while the activation energy of the diffusion becomes greater. The presence of polar groups and methyl groups in elastomers causes low rate of diffusion, which involves a great activation energy of diffusion. It is presumed that the activation energy of the diffusion is required to separate the rubber molecules for the displacement of the gas molecules. The attempt to elucidate the constant D_0 in the equation $D = D_0 \exp(-E/RT)$—which proves to be a function of the activation energy of the diffusion E—by reference to one of the formulas published in the literature failed. An empirical formula was derived whereby D_0 is directly related to the activation energy E.

ACKNOWLEDGMENT

In conclusion, I wish to express my thanks to the Rubber Foundation for permission to publish the results of the investigation; to A. van Rossem for his interest and advice; and to C. Zwikker for his collaboration in the preparation of the thesis, published in Delft in 1943, of which this paper reproduces a part.

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CORRELATION OF TENSILE STRENGTH WITH BRITTLE POINTS OF VULCANIZED DIENE POLYMERS *

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For several years work has been carried on here to evaluate a large number of diene polymers and copolymers as rubberlike materials. The writers have observed that changes in polymer composition which result in improved tensile strength and crack-growth resistance of the vulcanizate cause an increase in low temperature stiffness and a rise in brittle point. This generalization seems to apply to tensile values measured at elevated temperatures as well as to those at room temperature.

For example, a butadiene copolymer of dichlorostyrene can be made which, as a tread type of vulcanizate, exhibits a tensile strength of over 1500 pounds per square inch at 93° C, in comparison with 800 to 1000 pounds per square inch for GR-S in the same test tread formula at the same temperature. The brittle point of the butadiene-dichlorostyrene rubber, however, is −35° C or higher. GR-S treads in the same test have brittle points between −55° and −60° C. Probably of greater practical importance is the fact that the vulcanizate with the higher brittle point is stiffer at temperatures well above the brittle point.

The purpose of this investigation was to determine to what extent the maximum tensile strength of tread stocks of several synthetic rubbers varies with the temperature difference between the brittle point and the tensile testing temperature of each rubber. These data can then be used to judge the validity and extent of the general observation that changes in copolymer composition which increase strength also raise the brittle point.

PROCEDURE

Since many of the data presented here were collected over a period of several years, the compounding used for the tread test stock was not identical for all of the rubbers. They were alike, however, in that all contained either 45 or 50 parts of easy-processing channel black. The loading for each rubber is indicated in the tables. Tensile values reported by Tener, Kingsbury, and Holt[1] for Hevea over a wide range of temperatures and used here for comparison were for a tread containing 40 parts of an unspecified channel black.

Other ingredients in the 50-part-black compounds of the butadiene and isoprene copolymers (except those with vinylpyridine) were incorporated according to the Rubber Reserve test formula. The compound containing 45 parts of black is similar except that a combination of Captax and DPG is used in place of Captax alone, and sulfur is reduced from 2.0 to 1.6 parts. In the

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 38, No. 10, pages 1066–1070, October 1946. This paper was presented before the Division of Rubber Chemistry at the 109th meeting of the American Chemical Society, Atlantic City, N. J., April 9–12, 1946.

cases of rapid-curing copolymers of vinylpyridine and in the cases of Butyl and Neoprene, the other ingredients were markedly different for proper curing.

Tensile values were measured[2] over a range of cures for each compound on the Goodyear autographic machine at 27° C. Tests at higher temperatures were made on a standard L-2 Scott tester equipped with a heating jacket. Standard A.S.T.M. dumbbells, 1 × ¼ inch, were used on the Scott tester. The tensile value used in the present study was the highest observed over the range of cures.

Brittle point was determined by means of an impact test. Test specimens, 0.95 × 2.45 cm., are cut from standard test sheets 1.8 to 2.5 mm. thick. One end of the sample is clamped in the holder, and a piston is brought down sharply on the suspended end of the piece. The strips are tested in air in an aluminum cylinder surrounded by a dry ice–acetone bath. Temperature is lowered at the rate of approximately 1° per minute, and the blow is applied after each 5° C change. The temperature at which the piece shatters is recorded as the brittle temperature. The comparison in Table I of brittle points obtained by this method with those reported by Liska[3] shows satisfactory agreement.

DISCUSSION OF RESULTS

The data obtained, together with those of other workers used for comparison, are recorded in Table II. These data can be plotted on two separate graphs, room-temperature tensile against brittle point and hot tensile against

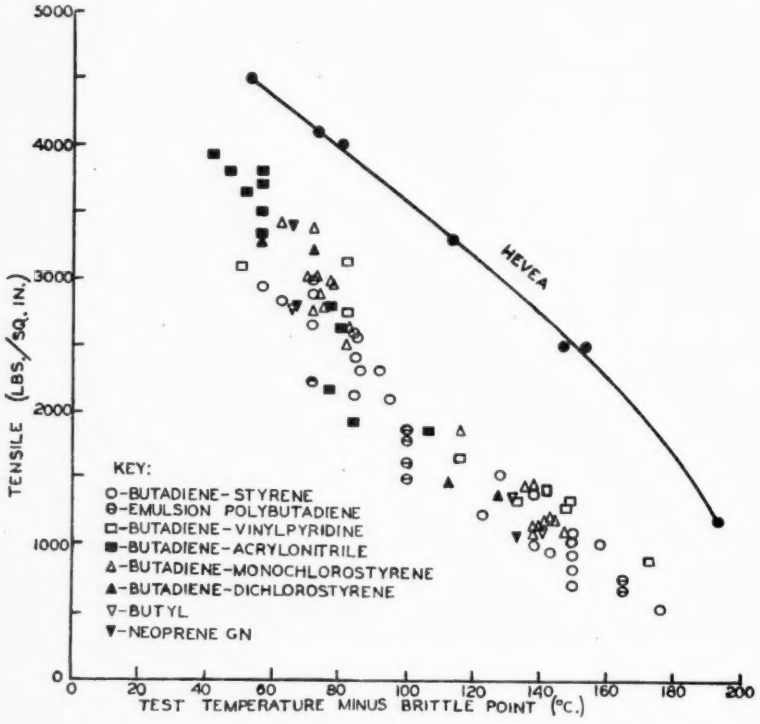

FIG. 1.—Tensile-brittle point comparison of tread stocks of Hevea and butadiene polymers.

TABLE I

COMPARISON OF BRITTLE POINT RESULTS WITH THOSE REPORTED BY LISKA[3] FOR TREAD COMPOUNDS

	Brittle Point (° C)	
	Goodyear	Liska
Natural rubber	−53	−53
Polybutadiene	−80	Below −72
75/25 butadiene/styrene	−57[a]	−63[a]
60/40 butadiene/styrene	−40	−42
Neoprene-GN	−40	−39
Butyl	−40	−39

[a] Our data for the copolymer containing approximately 24 per cent combined styrene; that of Liska probably an earlier sample containing 21–22 per cent styrene.

brittle point. It was considered preferable, however, to combine these two in one diagram to permit a test of the hypothesis that maximum tensile strengths of certain diene copolymers increase with a decrease in the temperature spread, ΔT, between the brittle point and the temperature at which the tensile measurement is made.

Figure 1 shows this comparison for butadiene polymers. In most instances there are two points for each polymer. One tensile value was determined at room temperature, hence, with ΔT values between 40° and 100° C; the second is the hot tensile with ΔT from 110° to 180° C. The points form a continuous band for the butadiene polymers, although the room-temperature tensile points for rubbers of low brittle point and the hot tensile values for polymers of high brittle point do not quite overlap.

In representing rubbers of several ratios of two comonomers, no distinction was made in the symbol. Thus, in Figure 1 butadiene/styrene copolymers from charged ratios of 90/10 to 50/50 are all represented by open circles. Each may be identified by reference to the values in Table II. One of the butadiene-styrene points represents data for a tread stock of German Buna S-3; it falls within the normal spread of the styrene rubbers.

With increase in the amount of vinyl compound in the butadiene copolymers, maximum tensile strengths increase and brittle points are higher. For a given proportion by weight, some vinyl monomers are more effective than styrene in improving tensile, but it is apparent that the sacrifice in brittle point is similar for a given degree of tensile improvement, regardless of the comonomer.

The band of points for butadiene polymers may be compared in Figure 1 with a curve for tensile values of a Hevea compound over a wide temperature range, reported by Tener, Kingsbury, and Holt[1]. Two additional points on this curve represent values obtained in this laboratory for a test compound containing 50 parts channel black[4]. The marked superiority of the tensile of Hevea over any butadiene rubber of comparable brittle point is evident. The spread between the band of points for the butadiene rubbers and the curve for Hevea indicates that, over a certain temperature range, Hevea exhibits tensile values 500 to 1400 pounds per square inch higher at the same ΔT than any of the synthetic rubbers tested.

Values for Butyl and Neoprene-GN are similar to those of the butadiene rubbers. Since these two polymers are fundamentally different, they are included in Figure 1 only for comparison.

TABLE II

SUMMARY OF TENSILE AND BRITTLE POINT VALUES

Rubber[a]	Black loading (parts/100 rubber)	Maximum tensile strength (lb./sq. in.)		Brittle point (° C)
		At room temp. (27° C)	At other temp.	
Polybutadiene	45	1625	765 (93° C)	−73
Polybutadiene	45	1500	700 (93° C)	−73
Polybutadiene	50	1800	..	−73
Polybutadiene	50	1870	..	−73
Butadiene/styrene				
90/10	50	2110	..	−68
85/15	45	2320	1020 (93° C)	−65
80/20	50	2310	..	−60
75/25	45	2600	940 (93° C)	−57
75/25	45	2370	715 (93° C)	−57
75/25	45	..	982 (86° C)	−57
75/25	45	..	840 (93° C)	−57
75/25	45	..	557 (119° C)	−57
75/25	45	2140	1030 (93° C)	−57
68/32 (Buna S-3)	45	2575	1125 (93° C)	−57
65/35	45	2650	1010 (93° C)	−45
65/35	45	2890	1410 (93° C)	−45
65/35	45	2245	..	−45
65/35	45	3000	..	−45
55/45	45	2850	1500 (93° C)	−35
50/50	45	..	1245 (93° C)	−30
50/50	50	2920	..	−30
Butadiene/acrylonitrile				
90/10	50	1905	..	−57
85/15	50	2680	..	−54
80/20	50	2800	..	−50
80/20	50	2180	..	−50
70/30	50	3300	..	−30
70/30	50	3700	..	−30
70/30	50	3800	..	−30
70/30	50	3500	..	−30
60/40	50	3650	..	−25
55/45	50	3800	1855 (93° C)	−20
50/50	50	3920	..	−15
Butadiene/dichloro-styrene, 75/25	50	3200	1365 (82° C)	−45
65/35	50	3275	1495 (82° C)	−30
Butadiene/*m*-chloro-styrene, 75/25	50	2500	1110 (93° C)	−55
70/30	50	2975	1205 (93° C)	−46
67/33	50	2800	1175 (93° C)	−45
65/35	50	3000	1095 (93° C)	−43
65/35	50	2750	1155 (93° C)	−43
65/35	50	3375	1445 (93° C)	−43
60/40	50	3400	1865 (82° C)	−35

TABLE II—*Continued*

Rubber[a]	Black loading (parts/100 rubber)	Maximum tensile strength (lb./sq. in.) At room temp. (27° C)	Maximum tensile strength (lb./sq. in.) At other temp.	Brittle point (° C)
Butadiene/mixed *o*- and *p*-chlorostyrenes				
80/20	50	2605	1030 (93° C)	−57
75/25	50	2975	1130 (93° C)	−51
70/30	50	2890	1125 (93° C)	−47
65/35	50	3000	1430 (93° C)	−43
Butadiene/vinylpyridine, 75/25	45	2750	1320 (93° C)	−55
75/25	45	3150	1305 (93° C)	−55
75/25	45	..	1437 (86° C)	−55
75/25	45	..	903 (119° C)	−55
65/35	50	..	1340 (93° C)	−40
55/45	45	3075	1675 (93° C)	−23
Polyisoprene	45	1300	545 (93° C)	−57
Polyisoprene	45	1550	780 (93° C)	−57
Polyisoprene	50	1230	480 (93° C)	−57
Isoprene/styrene, 75/25	45	2200	855 (93° C)	−29
75/25[11]	50	2500	1050 (93° C)	−29
75/25	50	1640	555 (93° C)	−29
50/50	45	2600	1065 (93° C)	−1
50/50[11]	50	2700	1440 (93° C)	−1
Isoprene/acrylonitrile				
80/20	50	1640	650 (93° C)	−29
70/30	50	1950	850 (93° C)	−12
67/33	50[b]	2630	..	−12
60/40	45	2240	1130 (93° C)	−7
Isoprene/methyl methacrylate, 75/25	45	1960	730 (93° C)	−34
Isoprene/vinylpyridine				
80/20	45	2420	990 (93° C)	−37
80/20	45	2460	1100 (93° C)	−37
75/25	45	2495	1010 (93° C)	−29
75/25	45	2380	1110 (93° C)	−29
75/25	45	2200	1200 (93° C)	−29
Hevea[4]	50	4000	2500 (93° C)	−53
Hevea[1]	40	..	5750 (−40° C)	−53
Hevea[1]	40	..	5050 (−20° C)	−53
Hevea[1]	40	..	4500 (0° C)	−53
Hevea[1]	40	..	4100 (20° C)	−53
Hevea[1]	40	..	3300 (60° C)	−53
Hevea[1]	40	..	2500 (100° C)	−53
Hevea[1]	40	..	1200 (140° C)	−53
Neoprene GN	45	2770	1070 (93° C)	−40
Neoprene GN	45	3400	..	−40
Butyl (GR-I)	45	2800	1375 (93° C)	−40

[a] Monomer ratio indicated is that charged into the polymerization reaction.
[b] SRF black.

Figure 2 represents a similar plot of tensile and ΔT values for a series of isoprene copolymers. In general, the points fall below those for the butadiene rubbers, and form a similar but broader band. Thus for a given brittle point, the isoprene rubbers are weaker than the butadiene polymers. The effects of vinyl comonomers on tensile and brittle point are the same as with the butadiene rubbers.

Preliminary data for polymers of 2-methyl-1,3-pentadiene from this laboratory and that reported by McMillan, Bishop, Marple, and Evans[5] show that these rubbers have still higher brittle points than butadiene or isoprene polymers, but are similar or inferior in tensile strength. In the Rubber Reserve test

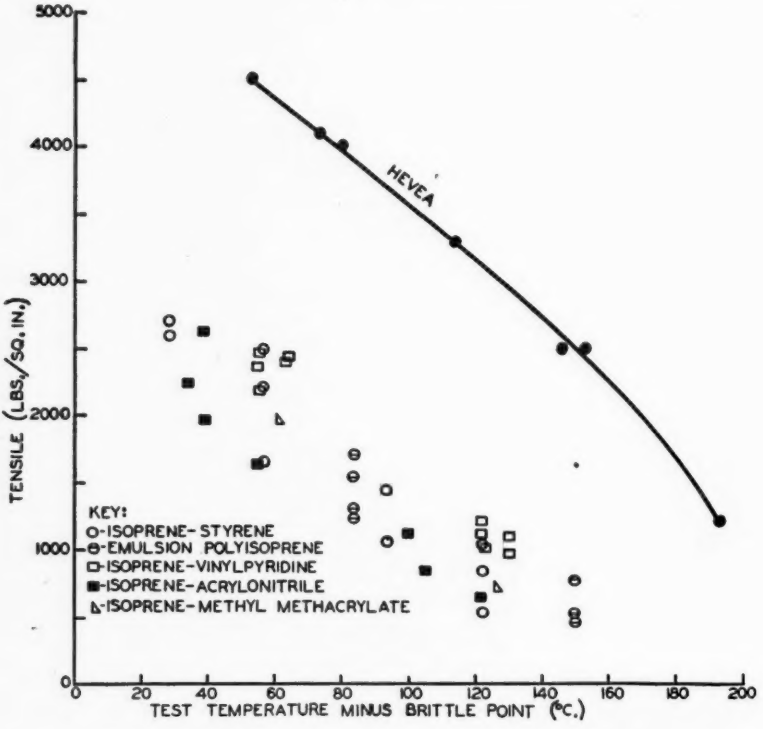

FIG. 2.—Tensile-brittle point comparison of tread stocks of Hevea and synthetic isoprene polymers.

formula, a methylpentadiene rubber had a tensile strength of 2150 pounds per square inch and a brittle point of −1° C. Hence the methylpentadiene rubbers tested are inferior with respect to the balance of tensile and brittle point properties.

METHOD OF POLYMERIZATION

All of the diene polymers and copolymers described here were made in emulsion. Polybutadienes and polyisoprenes formed by sodium-catalyzed mass polymerization have, in general, much higher brittle points than polymers of the same composition made in emulsion. This difference is illustrated in

Table III, which also includes data for polybutadienes reported by Conant and Liska[6]; they observed the higher brittle point of sodium-polymerized polybutadiene rubber.

TABLE III

BRITTLE POINTS OF EMULSION AND MASS POLYDIENES

Rubber	Compound	Brittle Point (° C)
GR-S	Tread	−57
Sodium butadiene/styrene[a]	Tread	−26
Emulsion polybutadiene	Tread	−73
Sodium polybutadiene	Tread	−51
Emulsion polybutadiene[6]	Gum	−74
Sodium polybutadiene[6]	Gum	−40

[a] Same butadiene/styrene ratio as GR-S.

Since these mass polymers of higher brittle point do not exhibit better tensile strengths than emulsion polydienes, their position on the graph of tensile against ΔT is below the bands shown in Figures 1 and 2. Polydienes prepared by other workers in this laboratory with organometallic catalysts were found to represent an improvement over sodium-catalyzed polydienes with respect to tensile–brittle point balance, but they were no better in this regard than rubbers made in emulsion.

If polydienes containing no second monomer are considered, changes in brittle point with method of polymerization probably depend on the structure of the polymer—*e.g.*, the number of side vinyl groups resulting from 1,2 addition of butadiene.

Selker, Winspear, and Kemp[7] found that polyisobutylene of very low molecular weight had a higher brittle temperature than polyisobutylenes of higher molecular weight, but that there was no significant change of brittle point for polymers beyond a molecular weight of about 10,000. Although polymers tested in the present investigation differ in average molecular weight and in molecular weight distribution, none were extremely low in molecular weight. The Mooney viscosity of the most plastic rubber included in this study was 26 (large rotor, 4 minutes, 100° C). In view of other experience in this laboratory and the discussion of Boyer and Spencer[8], it appears that structure rather than molecular weight must explain the differences in brittle point between mass and emulsion polydienes.

EFFECT OF PLASTICIZERS

The flexibility of rubber compounds may be improved by addition of suitable plasticizers. Although no thorough study has been made of the effect of plasticizers on the tensile–brittle point relation of the various rubbers, the data in Table IV summarize results of experiments in which dibutyl sebacate was added to a 50/50 butadiene/styrene copolymer.

Twenty parts of plasticizer lowered the brittle temperature from −30° to −45° C, which is still 12° higher than that for unplasticized GR-S. The maximum tensile strength of the plasticized 50/50 butadiene/styrene rubber had fallen to only 1650 pounds per square inch in comparison with 2320 for the GR-S control. Similarly the tensile of a tread stock of GR-S to which 20 parts of the same plasticizer had been added was only 1150 pounds per square inch. If values for these plasticized compounds are placed on the graph of Figure 1,

TABLE IV

TENSILE AND BRITTLE POINT VALUES OF PLASTICIZED BUTADIENE-STYRENE RUBBER TREAD COMPOUNDS

Rubber	Plasticizer (parts dibutyl sebacate)	Maximum tensile strength (lb./sq. in.)	Brittle point (° C)
50/50 butadiene-styrene	None	2650	−30
50/50 butadiene-styrene	20	1650	−45
GR-S	None	2320	−57
GR-S	20	1150	..

the points fall below the band for butadiene polymers. Thus, this particular plasticizer was less effective in lowering brittle temperatures with minimum loss of tensile than was a suitable change in copolymer composition.

GUM STOCKS

So far consideration has been given only to tread type of compounds containing 45 to 50 parts of channel black. It is appreciated that from a fundamental point of view it would be preferable to base this type of study on gum compounds or at least on stocks with lower loadings. Brittle temperatures of gum compounds differ only slightly from those reported here for black compounds. As is well known, however, tensile values of gum compounds of GR-S and other emulsion hydrocarbon diene polymers and copolymers are very low. Preliminary data indicate a relation between tensile and brittle point for the gum stocks which is similar to that observed for the loaded compounds. Again the vinyl monomers which increase the strength of rubber raise the brittle temperature, although the increase in strength may be from 220 to 450 pounds per square inch in a particular pair of gum compounds in comparison with a jump from 2400 to 2900 pounds for the loaded compounds of the same pair of rubbers. Difficulties in obtaining reliable stress-strain data for the weak gum compounds necessitate further measurements before valid conclusions are made.

Butyl and Neoprene, which fortuitously fell within the tensile–brittle point band for butadiene rubbers in the case of black compounds, have much higher gum tensile strengths than any butadiene or isoprene polymer of similar or even higher brittle temperature. Thus the three rubbers, Hevea, Butyl, and Neoprene, which can crystallize to some degree upon extension, excel the noncrystallizing butadiene and isoprene rubbers in the tensile–brittle point balance of their gum compounds. Of these three, only Hevea exhibits such a superiority in the tread compounds.

CORRELATION OF OTHER PROPERTIES WITH BRITTLE TEMPERATURE

A possible correlation with brittle temperature of test properties other than tensile strength reveals interesting general observations, but several difficulties arise in attempts to make quantitative comparisons.

For example, the same changes in copolymer composition that increase tensile strength and raise the brittle temperature ordinarily improve the resistance to crack growth of tread compounds of the copolymers. Since resistance to crack growth varies markedly with degree of cure, it is difficult to choose values at a comparable state of cure for a series of different synthetic

rubbers to permit a test of crack-growth relation to low temperature flexibility. Further study of both crack-growth resistance and tear resistance is planned.

In general, the emulsion polymers of highest resilience are those with the lowest brittle temperatures. Addition of a second monomer to butadiene, or increase of the amount of the second monomer, ordinarily lowers resilience and raises the brittle point of the copolymer. Such general observations hold for resilience measured at room temperature. At higher temperatures resilience of the copolymers increases and differences observed at room temperature between rubbers are reduced.

EFFECT OF TEMPERATURE ON TENSILE

The low tensile strength of GR-S compounds at temperatures near 100° C is well known. This observation has led to generalizations, such as that made by Parkinson[9], that "tensile and tear of carbon loaded GR-S compounds fall off much more rapidly with increasing temperature than do those of Hevea compounds". These generalizations have usually been based, however, on only two values, at room temperature and at approximately 100° C. It is of interest to observe the changes throughout this temperature range.

The Hevea data in Figure 3 are the same as those of Figure 1; GR-S values are from this laboratory for the compound containing 45 parts black. The slope of the curve in the room-temperature range is similar to that reported

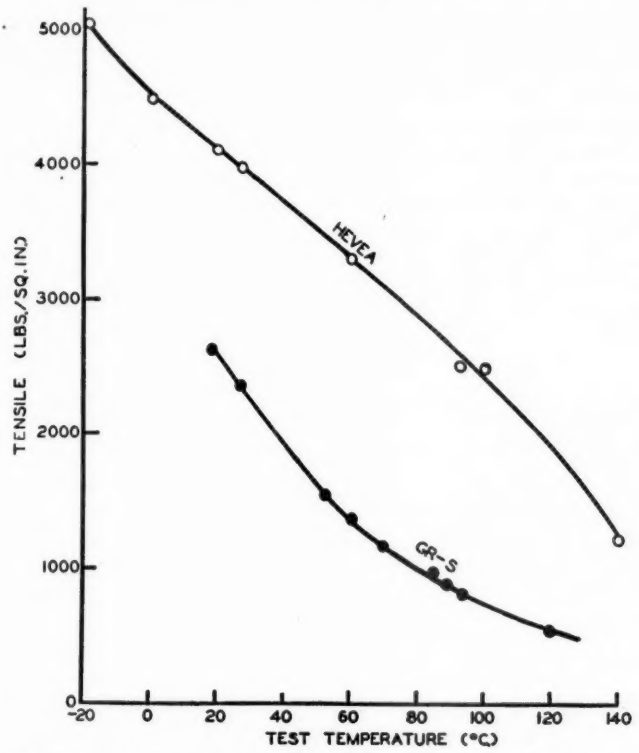

FIG. 3.—Effect of temperature on tensile strength of Hevea and GR-S tread stocks.

for GR-S by the National Bureau of Standards through the Office of the Rubber Director[10]. It appears that the rate of tensile decrease with increase of temperature is more rapid for the GR-S tread compounds than for Hevea at low temperatures. The curve for GR-S flattens at higher temperatures; that for Hevea begins to drop more rapidly near 120° C.

Statements concerning the more rapid loss of tensile of GR-S with increase in temperature are often based on percentage loss of the room-temperature tensile value. Even if the slopes of the two curves of Figure 3 were the same, the percentage loss of room-temperature strength would be greater for GR-S because of the low values at the low temperature. From a practical point of view the higher strength of Hevea compounds in the temperature range 70° to 120° C is the important consideration, rather than the rate of change of tensile over a particular range.

THEORY

It is possible that the structural features which restrict chain mobility at low temperatures also contribute to embrittlement or hardening of the rubber when elongated at the temperature of stress-strain measurements. Thus, those polymers of highest brittle point may harden most readily or to the greatest extent when they are stretched at room temperature. Since hardening might be expected to limit longitudinal slipping of chain segments, one might then predict a better distribution of stress and, hence, greater strength. Experimental studies to determine whether hardening actually occurs on stretching of noncrystallizing, synthetic butadiene and isoprene rubbers will be of interest.

ACKNOWLEDGMENT

The work reported here was done in connection with the Government Research Program of Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation. The authors are glad to acknowledge the coöperation of several members of the Goodyear Research Laboratories in preparing the polymers and of the Compound Development Department in compounding and evaluation. Particular thanks are due J. D. D'Ianni, J. H. Fielding, E. S. Teed, and R. M. Pierson. The permission of The Goodyear Tire & Rubber Company to publish this work is gratefully acknowledged.

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PROPERTIES OF HARD RUBBER. XIX. EFFECT OF TEMPERATURE ON CROSS-BREAKING STRENGTH AND ELONGATION *

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In a series of cross-breaking tests carried out on hard rubber during hot weather, the values of the breaking elongation[1] were higher than was expected, although the cross-breaking strength was of the usual order. It was thought that the high temperature might account for these results by making the hard rubber more plastic. The following experiments were, therefore, performed to investigate the effect of small changes of temperature, such as are encountered at different times of the year, on the cross-breaking strength and elongation.

Test-pieces of standard size (75 × 25 × 5 mm.) were cut from a sheet of hard rubber of the composition: 68 per cent rubber, 32 per cent sulfur, which had been vulcanized for 5 hours at 155° C. They were immersed in a beaker of water and kept at the required temperature for about 15 minutes, when they were judged to have attained a steady temperature. The tests were carried out on an Avery fabric-testing machine fitted with special clamps to give a three-point loading test, the distance between the supporting knife-edges being 50.4 mm. (2 in.)[2]. These clamps were heated to the temperature of the specimens by means of an electric radiator. The specimens were tested as soon as possible after they had been removed from the water, so that the change of temperature during the test was reduced as far as possible. The standard conditions already laid down[3], were observed.

The results for five test-pieces for each of the temperatures 12°, 15.5°, 20°, and 25° C are set out below.

Examination of the results indicates that the cross-breaking strength appears to decrease continuously from 1,352 kg. per sq. cm. at 12° C to 1,290 kg. per sq. cm. at 25° C, but the differences between the four means are not significant relative to the error of measurement.

The percentage elongation seems to increase very slightly with the temperature between 15.5° and 25° C. However, in view of the small magnitude of this increase relative to the error, and the fact that the value for 12° C does not fall into line with the other three, a definite conclusion on this point is not justified, and a much larger series of measurements is obviously needed before such a conclusion can be drawn.

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* Reprinted from the *Journal of Rubber Research*, Vol. 15, No. 12, pages 250–251, December 1946. Part XVIII appears in the *Journal of Rubber Research* Vol. 15, 179–180, August 1946 and in the January 1947 issue of RUBBER CHEMISTRY AND TECHNOLOGY.

CROSS-BREAKING STRENGTH AND ELONGATION

Specimen No.	Temp. (° C)	Elongation (%)	Strength (kg. per sq. cm.)
1	12.0	15.8	1281
2	12.0	16.6	1299
3	12.0	15.7	1356
4	12.0	15.8	1437
5	12.0	15.9	1376
	Mean	15.9	1352
6	15.5	14.1	1351
7	15.5	15.5	1347
8	15.5	13.9	1326
9	15.5	13.8	1349
10	15.5	15.1	1352
	Mean	14.5	1345
11	20.0	13.6	1352
12	20.0	15.4	1416
13	20.0	14.4	1375
14	20.0	15.4	1275
15	20.0	16.9	1268
	Mean	15.2	1337
16	25.0	16.4	1350
17	25.0	15.9	1241
18	25.0	15.7	1237
19	25.0	16.5	1252
20	25.0	14.7	1270
	Mean	15.8	1290

A decrease in the cross-breaking strength, similar in extent to that noted above, was observed by Hauser[4], who obtained the following results. No particulars of the composition or vulcanization of the hard rubber are given.

Temperature (° C)	8	23	36	46
Strength, kg. per sq. cm.	1110	1090	980	860

No figures for the corresponding elongations appear to have been reported.

Taking Hauser's results in conjunction with those tabulated above, there is a definite fall in cross-breaking strength with rise of temperature, in any event above about 20° C.

Although there are thus indications of the existence of appreciable temperature coefficients for the results of cross-breaking tests on an unloaded hard rubber, at least in the case of the cross-breaking strength, they are too small to affect seriously any measurements of the cross-breaking strength or elongation made within the normal range of room temperatures. It should be added that this conclusion relates to a material with a fairly high combined sulfur content (30.8 per cent). Materials with lower combined sulfur contents, on account of their greater plastic yield, may possibly be more influenced by variations in temperature.

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STATE OF CURE OF NEOPRENE VULCANIZATES

Measurement by the T-50 Test *

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Generally the physical properties of elastomer vulcanizates are considered to depend on their states of cure. Although many tests for measuring the state of cure have been developed, none are completely satisfactory. Some of them fail to distinguish between the physical or chemical effects of compounding ingredients, others are too laborious to be of practical value.

The T-50 test developed by Gibbons, Gerke, and Tingey[1] for natural rubber vulcanizates eliminates some of these difficulties and further reduces the number of tests required for production control. The T-50 test is based on the retraction of a stretched and frozen specimen with an increase in temperature. The temperature at which the sample retracts to 50 per cent of its initial frozen elongation is termed the T-50 value.

From a physical standpoint the test is sensitive, precise, and easily performed. From a chemical standpoint the original workers[1] as well as Vila[2] showed that, for any specific natural rubber composition, the T-50 value correlates with the amount of combined sulfur. Since the state of cure of a rubber vulcanizate is frequently discussed in terms of combined sulfur, the T-50 test offers a correlation of the state of cure with combined sulfur without the necessity for involved chemical analyses.

In the case of Neoprene vulcanizates, no correlation between state of cure and a chemical property is known. For this reason it might be expected that the T-50 test would not be applicable to determinations of the state of cure of Neoprene vulcanizates. Reports by the Naugatuck Chemical Division of the U. S. Rubber Company[3] and by Cohan and Steinberg[4] indicate that the T-50 test probably is not adaptable to measurements of the state of cure of all vulcanized elastomers. Only one report on the use of a T-50 type test with Neoprene compounds is known. This was made by Yerzley and Fraser[5], who described a retraction-temperature test as one of several which could be used for estimating the freeze resistance of elastomer vulcanizates.

In the case of natural rubber vulcanizates, extensive retraction occurs within very narrow temperature limits near the T-50 point. The precision of the measurement of this point is therefore high. An analysis of the work of Yerzley and Fraser[5] showed that this is not true for Neoprene vulcanizates, and that measurements of the T-50 point only are not so precise or significant as they are with natural rubber. For this work, therefore, the T-50 test was extended to include temperature measurements, not only at the point of 50 per cent retraction, but also at other 10 per cent intervals between 10 and 90 per cent retractions. Smooth curves that are often S-shaped are obtained by plotting the

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 38, No. 10, pages 1048–1052, October 1946. This paper was presented before the Division of Rubber Chemistry at the 109th meeting of the American Chemical Society at Atlantic City, N. J., April 9–12, 1946.

percentage retractions as ordinates and the temperatures as abscissas. These curves show the greatest sensitivity between 30 and 70 per cent retractions; therefore, in comparing Neoprene compounds for changes in their state of cure, it is more satisfactory to consider the complete retraction-temperature curves rather than the single T-50 values. Changes in the slopes and the positions of the curves are indicative of changes in the state of cure. The T-50 values have been found to be reproducible with an accuracy of ±1° C and have been selected as a reference point. The T-50 values on the retraction curves are suitable for controlling the manufacture of Neoprene products as well as for expediting laboratory investigations. Hence, they are applicable to Neoprene compounding in much the same way that the conventional T-50 measurements are applicable to the compounding of natural rubber. Although the work described is restricted to tests on Neoprene Type GR-M, supplementary tests have shown that this test is equally applicable to other types—for example, Neoprene Type FR and Neoprene Type CG.

TEST PROCEDURES

Except as described here, the test procedures conformed to established A.S.T.M. methods[6]. The specimens were mounted in a special T-50 type holder, fitted with a graduated scale for measuring retractions at 10 per cent intervals. As the holding apparatus was designed to hold samples at given elongations, the tests were run on specimens stretched 170, 270, and 340 per cent. Accordingly, the results are based on these elongations rather than 50 per cent of the breaking elongations as recommended by Gibbons, Gerke and Tingey[1]. After mounting, the samples were stretched and then conditioned 10 minutes in an alcohol bath at 20° C. The temperature was then lowered at a rate of 2° C per minute by a circulating acetone–carbon dioxide system until −40° C was reached. The samples were held at −40° for 10 minutes, and the temperature was then lowered 1° C per minute until −70° C was reached. The samples were held at −70° for 10 minutes and then released for retraction. Finally the temperature was raised 1° per minute, and readings were taken at each 10 per cent interval of retraction through 90 per cent.

Table I gives the Neoprene compositions described in this paper, and their physical tests are shown in Table II.

TABLE I

FORMULAS OF NEOPRENE GR-M COMPOUNDS

Compound No.	A	B	B-1	B-2	B-3	C	C-1	C-2	C-3
Neoprene GR-M	100	100	100	100	100	100	100	100	100
Stearic acid	..	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Neozone A[a]	..	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Extra-light calcined magnesia	7.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
MT carbon black	..	..	..	..	..	57.6	57.6	57.6	57.6
SRF black	..	28.8	28.8	28.8	28.8	..	..	..	..
Permalux[b]	..	..	..	..	1.0	..	..	..	..
Sulfur	..	..	1.0	2.0	..	..	1.0	..	..
Tributoxyethyl phosphate	..	..	..	..	..	..	..	30.0	..
Tricresyl phosphate	..	..	..	..	..	..	..	..	30.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0

[a] Phenyl-α-naphthylamine.
[b] Di-o-tolylguanidine salt of dicatechol borate.

T-50 VALUES AND STATE OF CURE

Several of the more important factors affecting the state of cure of Neoprene vulcanizates are considered in the following paragraphs. The relations be-

TABLE II

PHYSICAL PROPERTIES OF NEOPRENE GR-M COMPOUNDS

Compound No.	Cure		Stress at 300% (lb./sq. in.)	T_B(lb./sq. in.)	Elongation (%)	Shore hardness
	Time (min.)	Temp. (° C)				
A	30	142	300	3975	1025	46
B	60	108	250	750	890	55
	15	142	850	2525	880	55
	30	142	975	2450	740	56
	60	142	1175	2650	665	56
	120	142	1375	2625	540	60
	10	153	1200	2900	780	56
	60	153	1350	2650	545	60
B-1	60	153	1875	2400	380	66
B-2	60	153	2250	2550	340	68
B-3	10	153	1625	2700	545	61
C	30	142	825	1850	700	56
	40	153	650	1650	540	61
C-1	10	153	925	1700	645	55
	120	153	1750	1950	385	66
C-2	40	153	325	1550	680	36
C-3	40	153	400	1575	730	40

tween these factors and T-50 values are discussed. For convenience, cross lines have been drawn on the graphs at the point where the T-50 value is 0° C.

Effect of Curing Time and Temperature.—The fundamental differences in the retraction temperatures of vulcanizates having varying states of cure are illustrated in Figure 1. The retraction curves shift to the left, and specific T-values become lower as the time or temperature of cure increases. Accordingly, retraction temperatures decrease as the state of cure is increased. In general, the greatest differences between two or more retraction curves lie between 30 and 70 per cent recoveries.

Effect of Acceleration.—The curves of Figure 2 show the increase in the state of cure of a Neoprene composition caused by the addition of an accelerator such as the di-*o*-tolylguanidine salt of dicatechol borate (Permalux). A further example of the use of temperature retraction curves as a method of evaluating acceleration is brought out by comparing the curves of Figures 1 and 2. The T-50 value of the stock containing 1 per cent Permalux, cured 10 minutes at 153° C (Figure 2), is approximately equal to the T-50 value of the control stock containing no Permalux, cured 120 minutes at 142° C (Figure 1). This indicates that these vulcanizates have essentially the same state of cure; the stress-strain data of Table II confirm this by showing that the properties of these vulcanizates are nearly equal.

Effects of Loading.—Figure 3 shows great differences between the retraction curves of a gum vulcanizate and those of two carbon black vulcanizates. Although the magnesia–zinc oxide ratio of compound A differs from those of compounds B and C, unpublished data obtained in this laboratory have shown that these differences would not affect the relations between these compounds. Therefore, measurement of T-values may be an excellent method for determining the effects of different fillers on the rate of cure of Neoprene GR-M.

Effects of Plasticizers.—Stress-strain properties, compression set tests, resilience data, etc., do not provide a clear distinction between the physical

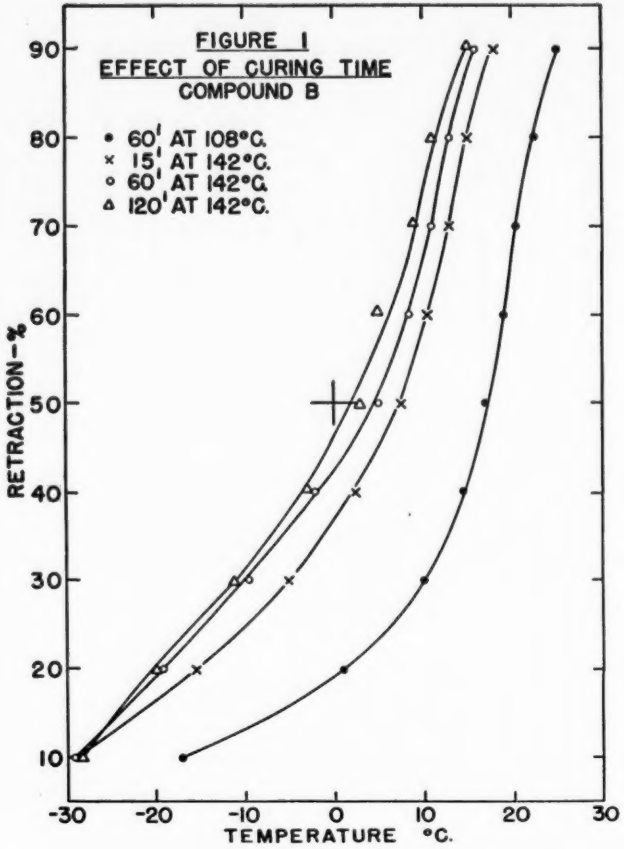


FIGURE 1
EFFECT OF CURING TIME
COMPOUND B
• 60' AT 108°C.
× 15' AT 142°C.
○ 60' AT 142°C.
△ 120' AT 142°C.
RETRACTION-%
TEMPERATURE °C.

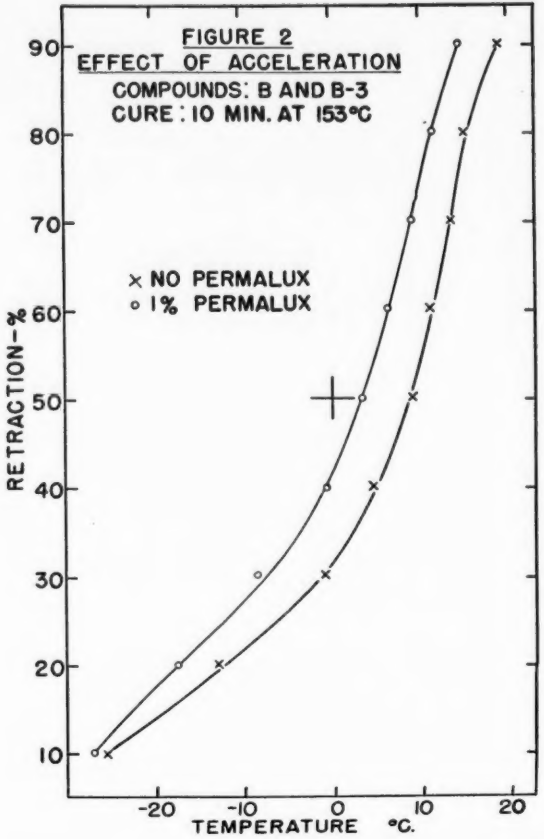


FIGURE 2
EFFECT OF ACCELERATION
COMPOUNDS: B AND B-3
CURE: 10 MIN. AT 153°C
× NO PERMALUX
○ 1% PERMALUX
RETRACTION-%
TEMPERATURE °C.

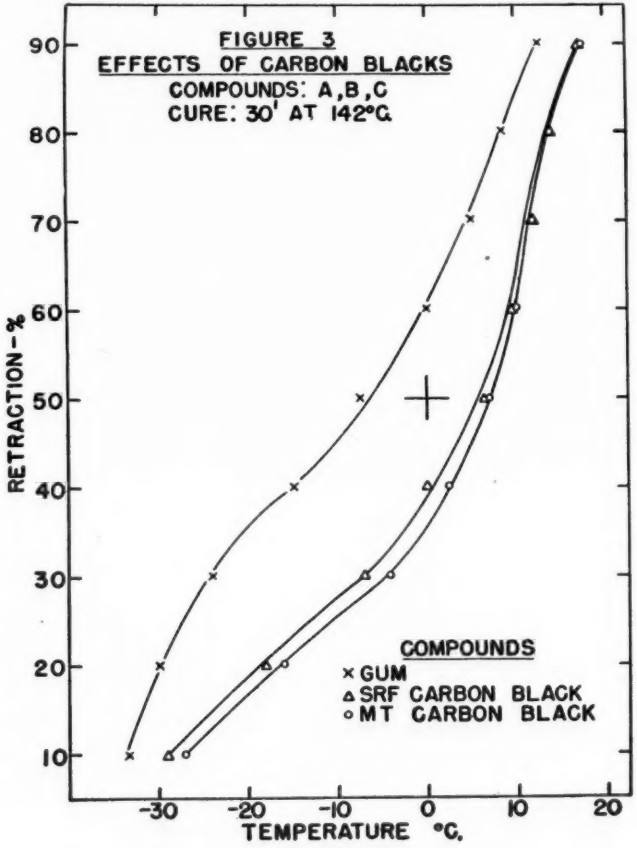


FIGURE 3
EFFECTS OF CARBON BLACKS
COMPOUNDS: A, B, C
CURE: 30' AT 142°C.
RETRACTION - %
TEMPERATURE °C.
COMPOUNDS
× GUM
△ SRF CARBON BLACK
○ MT CARBON BLACK

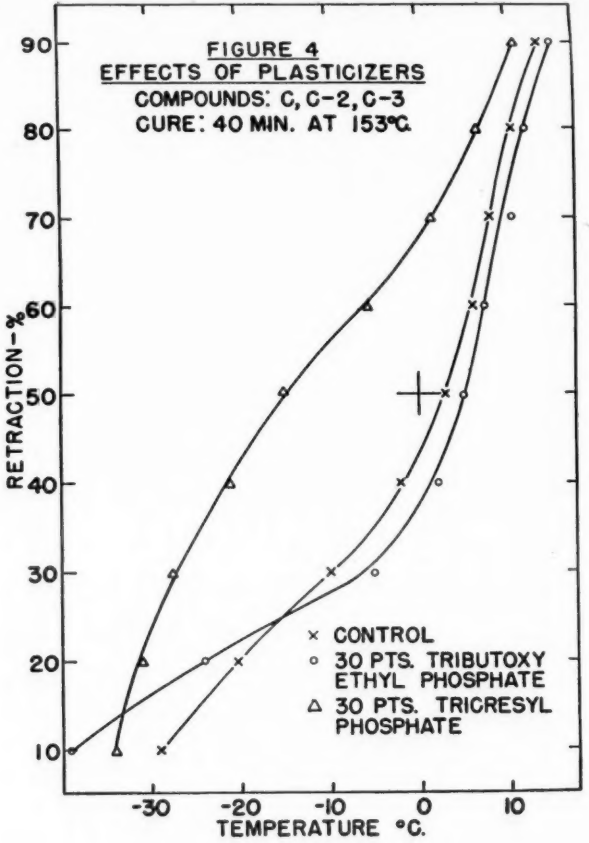


FIGURE 4
EFFECTS OF PLASTICIZERS
COMPOUNDS: C, C-2, C-3
CURE: 40 MIN. AT 153°C.
RETRACTION - %
TEMPERATURE °C.
× CONTROL
○ 30 PTS. TRIBUTOXY ETHYL PHOSPHATE
△ 30 PTS. TRICRESYL PHOSPHATE

and chemical effects of plasticizers. For example, there is little difference in the stress-strain properties of compounds C-2 and C-3 (Table II) which contain equal quantities of tributoxyethyl phosphate and tricresyl phosphate, respectively. The T-50 test appears to be a method of measuring the chemical effects of added plasticizer. Figure 4 compares the complete temperature-retraction curves of Neoprene stocks containing tributoxyethyl phosphate and tricresyl phosphate with a control stock containing no plasticizer. The temperature-retraction curve for the tricresyl phosphate compound indicates that this plasticizer has a definite activating effect. The temperature-retraction curve for the tributoxyethyl phosphate compound has an abnormal shape, and the same phenomenon has been observed with several different plasticizers. As judged by the higher end of the curve—that is, 25–90 per cent retractions—tributoxyethyl phosphate produces a mild retarding effect. The lower end of the curve—below 25 per cent retraction—crosses the curve of the control stock. This is believed to be caused by physical effects which are somewhat independent of the state of cure.

Unusually low T-10 values (temperature of 10 per cent retraction) were observed in some stocks containing plasticizers which were added to improve freeze resistance[7]. These low T-10 values can be correlated with such freeze resistance tests as brittle points and hardening during short exposures to very low temperatures. Plasticizers that have produced the best freeze resistance have also produced the lowest T-10 values. Since tributoxyethyl phosphate is known to be an excellent plasticizer for improving freeze resistance[7], we can expect that its compounds would show lower than normal temperatures for lower retractions.

Based on T-50 values, Table III classifies several other plasticizers with respect to their accelerating or retarding tendencies.

TABLE III

EFFECT OF PLASTICIZERS ON STATE OF CURE

Plasticizer	Amount[a]	T-50 value (° C)	Effect on cure
Cured 30 minutes at 142° C			
Control (compound C)	..	+ 7	..
Circo process oil	15	0	Accelerates
Dioctyl sebacate	15	+ 4	Accelerates
Flexol 3GO[b]	15	+ 7	Neutral
Flexol 4GO[c]	15	+ 7	Neutral
Flexol DOP[d]	15	+ 0.5	Accelerates
Cured 40 Minutes at 153° C			
Control (compound C)	..	+ 3	..
Circo process oil	15	− 3	Accelerates
Circo process oil	30	−15	Accelerates
Dibutyl sebacate	15	+ 2.5	Neutral
Dicapryl phthalate	30	−13	Accelerates
Tributoxyethyl phosphate	30	+ 5	Retards
Flexol 3GO	30	− 1	Accelerates

[a] Plasticizer added to control composition.
[b] Triethylene glycol do-2-ethylhexoate.
[c] Polyethylene glycol di-2-ethylhexoate.
[d] Di-2-ethylhexyl phthalate.

STATE OF CURE AND CRYSTALLIZATION

The time-consuming tests required to measure hardness or modulus increases caused by the crystallization of Neoprene vulcanizates at moderately low temperatures[8] can be partially eliminated by determining the T-50 temperature. Since both T-50 temperatures and crystallization tendencies depend on state of cure, it was assumed that vulcanizates having certain T-50 values would not crystallize. It has been observed that Neoprene compositions containing filler and no plasticizer have little or no tendency to crystallize if the T-50 temperature is below −5° C. Figures 5 and 6 and Table IV show

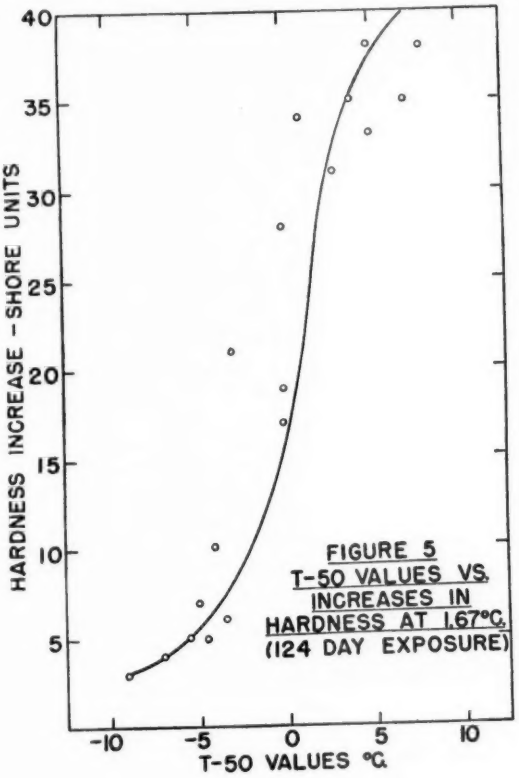


FIGURE 5
T-50 VALUES VS. INCREASES IN HARDNESS AT 1.67°C. (124 DAY EXPOSURE)

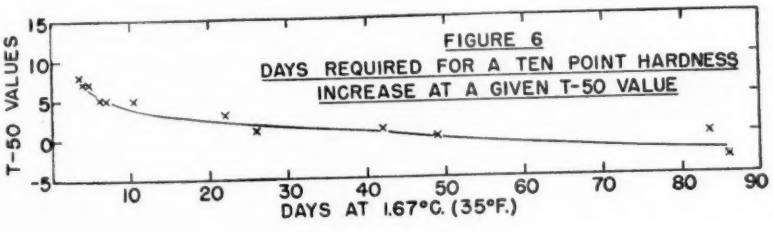
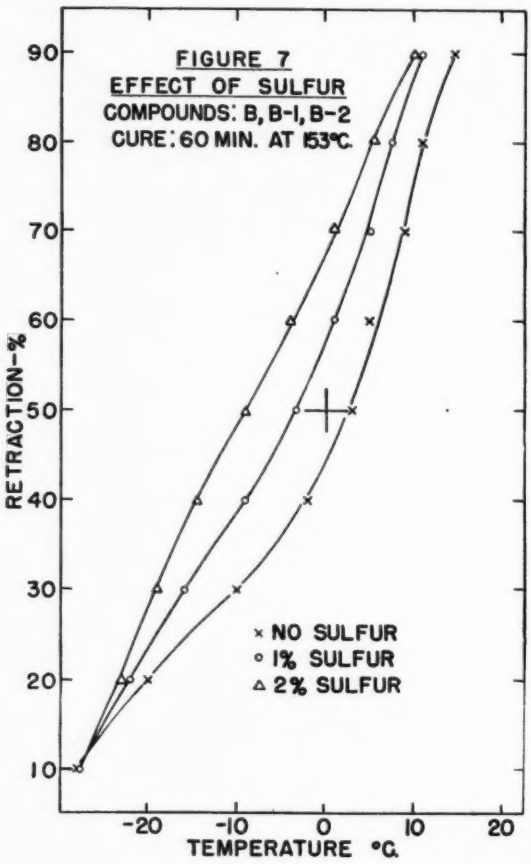


FIGURE 6
DAYS REQUIRED FOR A TEN POINT HARDNESS INCREASE AT A GIVEN T-50 VALUE

the relation between T-50 values and increases in hardness during long exposures at 1.67° C. Sulfur vulcanization, which prevents the crystallization of Neoprene GR-M[9], has a pronounced effect on T-50 values. The effects of 1 and 2 per cent added sulfur are shown in Figure 7, which compares compounds



B, B-1, and B-2. At a given cure (60 minutes at 153° C) the T-50 value decreases from +3° to −9° C as the sulfur content is increased from 0 to 2 per cent. Available data are insufficient to show whether the combined sulfur in Neoprene vulcanizates can be estimated from T-50 measurements.

EFFECTS OF TEST ELONGATION

Actual T-50 values of specific Neoprene compositions, like those of natural rubber vulcanizates, depend on the elongation applied to the test specimen. Table V shows the differences in the T-50 values of compound C-1 when two cures, 10 and 120 minutes at 153° C, were tested at elongations of 170, 270, and 340 per cent. The overall differences in the retraction curves are shown in Figure 8. This analysis indicates that it should not be necessary to test Neo-

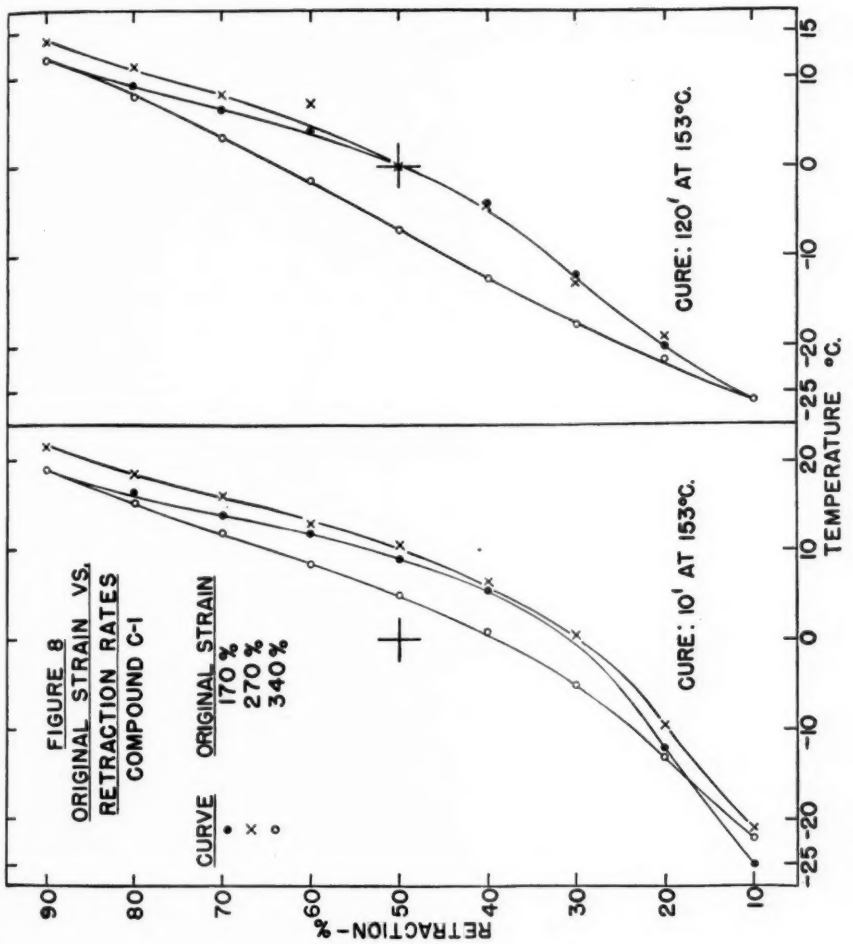


FIGURE 8
ORIGINAL STRAIN VS.
RETRACTION RATES
COMPOUND C-1
CURVE ORIGINAL STRAIN
• 170 %
× 270 %
○ 340 %
CURE: 10' AT 153°C.
CURE: 120' AT 153°C.
RETRACTION - %
TEMPERATURE °C.
90
80
70
60
50
40
30
20
10
-25 -20 -10 0 10 20 -25 -20 -10 0 10 15

prene compositions at a given percentage of their ultimate elongations. Relations between test-specimens are similar for each test elongation used. Therefore, in using the T-50 test for control or development work, any given elongation should be satisfactory for testing most vulcanizates.

TABLE IV

RELATION BETWEEN T-50 VALUES AND STIFFENING

Specimen No.[a]	Cure at 153° C (min.)	T-50 value (° C)	Increase in hardness at 1.67° C (35° F)				
			4 days	10 days	36 days	56 days	124 days
1	20	−3	0	3	3	6	21
	60	−5.5	0	1	2	3	5
2	20	+5	1	25	34	33	35
	60	+1	0	6	27	31	34
3[b]	20	+5	1	9	29	31	33
	60	+3	0	4	21	28	31
4[c]	20	0	0	3	6	11	17
	60	−3.5	1	3	3	4	6
5[d]	20	0	0	3	4	6	19
	60	−9	0	2	1	2	3
6	20	−4.5	0	3	2	2	5
	60	−9	0	2	1	3	3
7	20	+7	8	33	38	39	40
	60	+5	2	23	35	36	38
8	20	+1	0	4	6	14	28
	60	−4	1	5	4	5	10
9	20	+8	12	33	35	36	38
	60	+7	7	26	32	33	35
10	20	+5	0	26	29	32	33
	60	+4	0	10	30	34	35
11	20	−5	0	2	1	3	7
	60	−7	0	2	1	2	4

[a] Some of the compositions listed are in addition to those in Table I, and were used in a study of crystallization conducted in this laboratory; none contained plasticizers.
[b] Same as compound B, Table I.
[c] Same as compound B-1, Table I.
[d] Same as compound B-2, Table I.

TABLE V

RELATION BETWEEN INITIAL STRAIN AND T-50 VALUES

Cure at 153° C (min.)	Ultimate elongation resulting from following test elongation:			T-50 values (° C)		
	170%	270%	340%	170%	270%	340%
10	25.6	40.6	51.1	+9	+10.5	+5
120	48.6	77.2	97.2	0	0	−7

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MECHANICAL PROCESSING OF CARBON BLACKS

Resultant Effects in GR-S Compounds

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Recent publications[1] concerning the behavior of carbon black in GR-S compounds described a group of carbons as "structure carbons". These blacks are characterized by their ability to impart smoothness to uncured stocks at normal tread stock loading, and high modulus to cured compounds. Such properties were attributed to structure-forming tendencies—that is, to the ability of the carbon particles to maintain a chain-like grouping (illustrated in Figure 1 as a secondary aggregate) when dispersed in rubber media, as contrasted

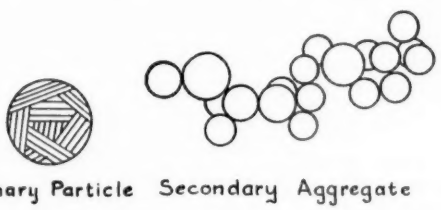

FIG. 1.—Possible configuration of carbon black aggregate made up of primary carbon black particles.

with nonstructure blacks, which tend to disperse as single discreet particles. The structure of the primary particle was thoroughly defined by x-ray diffraction studies[2]. No theoretical interpretation has been offered to describe rigidly the contribution of structure to modulus; it was found necessary to introduce a particle-shape factor to account for modulus characteristics of carbon blacks[3].

Shawinigan acetylene black is a commercial carbon black exhibiting high modulus which has been attributed to a high structure tendency. However, it seems reasonable to assume that structure is not a property unique to any single type of carbon black but is possessed to some degree by all blacks. Modulus properties of a black may be taken as some indication of the extent of structure.

It is difficult to demonstrate the existence of this structural tendency. The electron microscope offers the best direct evidence of the chainlike grouping of particles[4]. The most striking evidence of this type has been demonstrated with acetylene black[5]. The fact that acetylene black resists compression and is difficult to densify or pelletize is further evidence of the existence of secondary aggregates in this material. It was of interest, therefore, to determine whether mechanical treatment could alter or destroy this association among individual particles responsible for structure, and thus permit densifica-

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 38, No. 11, pages 1145–1148, November 1946. This paper was presented before the Division of Rubber Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, N. J., April 10–12, 1946.

tion or pelletization of the black. Furthermore, it was hoped that if such treatment could be correlated with rubber properties, it might offer further evidence in support of the structure theory of high modulus blacks.

MECHANICAL TREATMENT

Shawinigan acetylene black used in the experiments had an initial bulk density of 2.8 pounds per cubic foot. One-half pound of this material was compressed by a hydraulic ram to a density of 30 pounds per cubic foot and held at this density for 17 hours. The pressure was then relieved and the black removed from the chamber. The large lumps were brushed through a No. 28 U. S. Standard sieve. The bulk density after sieving was 18.4 pounds per cubic foot. In a second experiment 2 pounds of the original fluffy black were milled with flint pebbles for 3 hours. The bulk density at the end of this time was 19.1 pounds per cubic foot. Finally, half of this dense pebble milled black was subjected for 90 minutes to the mechanical pelletizing action of a standard Spheron process apparatus[6]. Small, firm pellets were formed in this operation, ranging in sieve size between 28 and 60 mesh. These pellets had a bulk density of 23.1 pounds per cubic foot.

Thus, three samples were prepared with bulk densities of 18, 19, and 23, respectively, in contrast to the original density of 2.8 pounds per cubic foot. This change was accomplished by straight application of pressure and by vigorous and continued mechanical action.

ANALYTICAL PROCEDURE

Surface areas were determined by the low temperature, nitrogen-adsorption isotherm technique of Brunauer and Emmett[7]. Diphenylguanidine adsorption was determined by the method of Amon and Estelow[8]. The Gardner method was used for measuring oil absorption. The values are expressed in pounds of oil required to wet 100 pounds of black[9]. Carbon tetrachloride retention values were determined by the method described by Hall, Buckley, and Griffith[10]. pH value was determined according to the method described by Wiegand[11].

Heat of adsorption measurements (Figure 2) on the original and densified material were carried out at $-196°$ C, using nitrogen as the adsorbate. Relative blackness of the samples was determined by the nigrometer[12]. Electrical resistance of the black was determined by measuring the resistance of a column of black 1 inch high and 0.75 inch in diameter under a pressure of 150 pounds per square inch.

DISCUSSION

The mechanical processing experiments were successful in permanently overcoming resistance to compression, and resulted in a pelletized material of high density. This result suggested that the secondary aggregates in acetylene black had been altered or destroyed.

Table I shows decreasing oil adsorption, carbon tetrachloride liquid retention, and electrical resistance with increasing density or continued mechanical treatment. These decreasing values are due to the increased apparent density. It is suggested that this closer packing or increased density is accompanied by a destruction of the structure units depicted as secondary aggregates in Figure 1. In previous publications both oil adsorption and carbon tetrachloride liquid retention tests were used as a measure of structure[10].

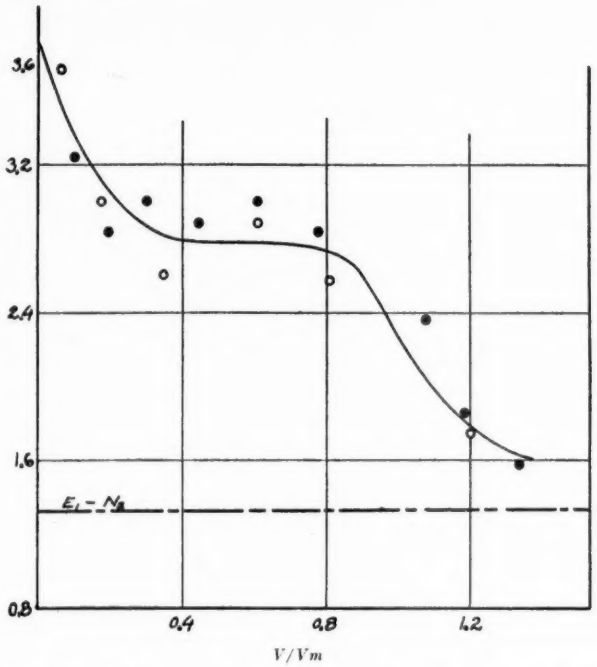

FIG. 2.—Differential heat of adsorption curve of fluffy black and ball-milled, pelletized material.
○ Acetylene black
● Acetylene black, ball-milled and pelletized.

TABLE I

EFFECT OF MECHANICAL TREATMENT ON ANALYTICAL PROPERTIES OF CARBON BLACK

Sample	Density (lb. per cu. ft.)	Oil adsorption (lb. per 100 lb. black)	CCl_4 (cc. retained per 5 g. black)	Electrical resistance
Fluffy acetylene black	2.8	161	30.4	0.194
Heavy compressed	18.4	121	9.1	0.170
Ball-milled	19.1	87	6.9	0.160
Ball-milled and pelletized	23.1	85	5.9	0.160

The decrease in nigrometer index (Table II), indicating increasing blackness[12], is a superficial result and is due to the significant decrease in oil adsorption. The nigrometer index is a measure of blackness of a carbon black-oil

TABLE II

EFFECT OF MECHANICAL TREATMENT ON ANALYTICAL PROPERTIES OF CARBON BLACK

Sample	Density (lb. per cu. ft.)	Nigrometer index[a]	Surface area (sq. m. per g.[b])	pH	D.P.G. adsorption (%)
Fluffy acetylene black	2.8	93.8	69	7.4	0.46
Heavy compressed	18.4	92.1	68	6.3	10.8
Ball-milled	19.1	90.8	70	5.7	18.1
Ball-milled and pelletized	23.1	90.8	75	5.7	16.8

[a] Relative blackness increases as index decreases.
[b] Surface area by Brunauer and Emmett[7], N_2-adsorption method.

mix. It was found that, as the excess oil in the mix increases, the index decreases. Surface area shows only a slight increase outside of the range of error in the measurement. The interpretation of these two measurements confirms that no large or significant change in particle size occurred. There is, however, some indication of change in the nature of the surface of the black, judging from the increase in diphenylguanidine (D.P.G.) adsorption index, and decreasing pH values[13].

On the other hand, Figure 1 shows that no change in the heat of adsorption of nitrogen between fluffy acetylene black and the final pelletized product occurred; this suggests that the surface forces are essentially unchanged.

Thus, results of mechanical processing suggest that secondary aggregates were altered or destroyed. Analytical data, particularly electron-microscope pictures (Figures 3 and 4), oil absorption measurements, and liquid retention measurements confirmed this suggestion. This study of structural properties is therefore extended to an investigation of the properties of rubber stocks containing these blacks.

The samples were compounded in a standard GR-S recipe (Table III) employing a laboratory Banbury mixing procedure.

TABLE III

RUBBER FORMULA

Ingredient	Parts by weight
Rubber	100
Carbon black	50
Zinc oxide	5
Santocure	1
Sulfur	2
Pine tar	3
Bardol	5

To ensure that results for any given test series would be strictly comparable, the following precautions were carried out: (1) Use was made of thoroughly blended GR-S; (2) sulfur and zinc oxide–Santocure master batches were used; and (3) individual cures (30, 60, and 90 minutes) were made simultaneously on all samples in a given test series. However, test series on different commercial carbons were carried out on different dates. Therefore test results among different commercial carbon samples are not strictly comparable.

When the stocks containing the acetylene black samples were sheeted out on the roll mill, they showed a definite and progressive decrease in both length and relative smoothness with extent of mechanical treatment. This effect is illustrated in Figure 5. Microscopic examination of the rubber stocks, employing the Allen squeeze-out technique, showed no differences in gross dispersion of the black.

Cures were made at 292° F, and, at the end of each cure, the samples were quenched in a water bath and allowed to age in air overnight at 80° F before testing. Rubber test data are presented in Table IV.

The modulus values at full cure show a definite and progressive decrease relative to the extent of mechanical treatment. Ultimate tensile strength, however, shows no significant change. The electrical resistance values of the cured stock at 60-minute cure show a progressive increase with extent of mechanical treatment. Thus it is evident that all changes in the properties of compounded GR-S, believed to be related to the presence of secondary aggre-

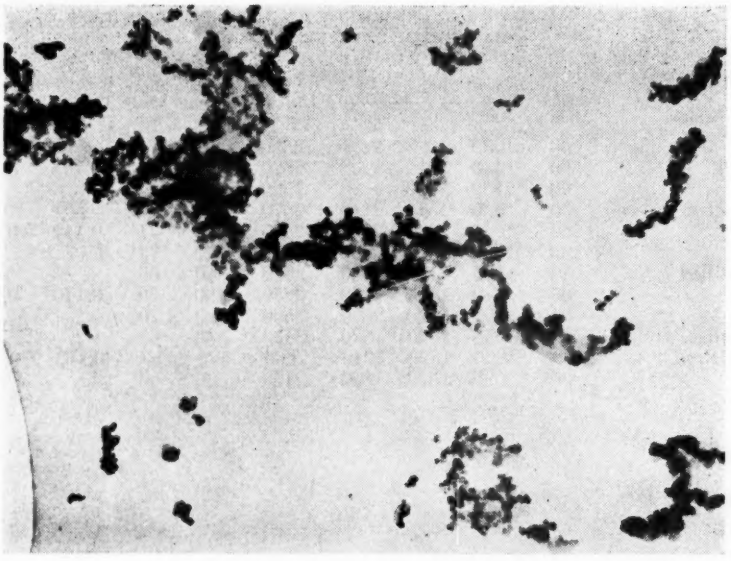

FIG. 3.—Electron microscope picture of original fluffy acetylene black (×21,500).

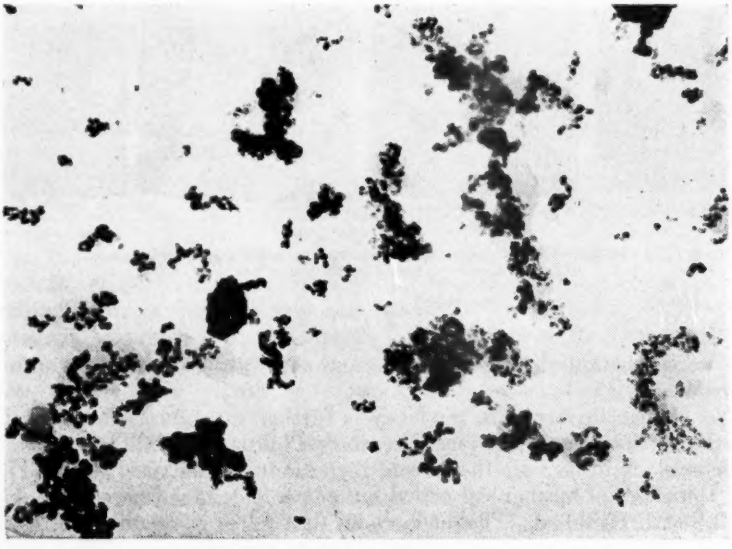

FIG. 4.—Electron microscope picture of same acetylene black after mechanical treatment (×22,300).

TABLE IV

EFFECT OF MECHANICAL TREATMENT ON RUBBER PROPERTIES OF SHAWINIGAN ACETYLENE BLACK

Sample	Cure at 292° F (min.)	Modulus 200%	Modulus 300%	Modulus 400%	Ultimate tensile	Elongation (%)	Shore hardness	Torsional hysteresis	Electrical resistance
Fluffy acetylene black	30	1030	1690	2290	2550	450	71	..	..
	60	1230	2010	..	2520	390	73	0.148	0.0011
	90	1180	2000	..	2520	390	74	..	..
Heavy compressed	30	860	1570	2140	2670	490	69	..	..
	60	1040	1840	2440	2590	420	71	0.142	0.0018
	90	1060	1800	2390	2590	420	72	..	..
Ball-milled	30	570	1150	1650	2620	580	66	..	..
	60	810	1460	2090	2250	480	69	0.140	0.0027
	90	800	1470	2090	2560	400	70	..	..
Ball-milled and pelletized	30	510	1040	1520	2470	580	66	..	..
	60	690	1320	1940	2660	520	68	0.153	0.0035
	90	690	1320	1890	2450	480	69	..	..

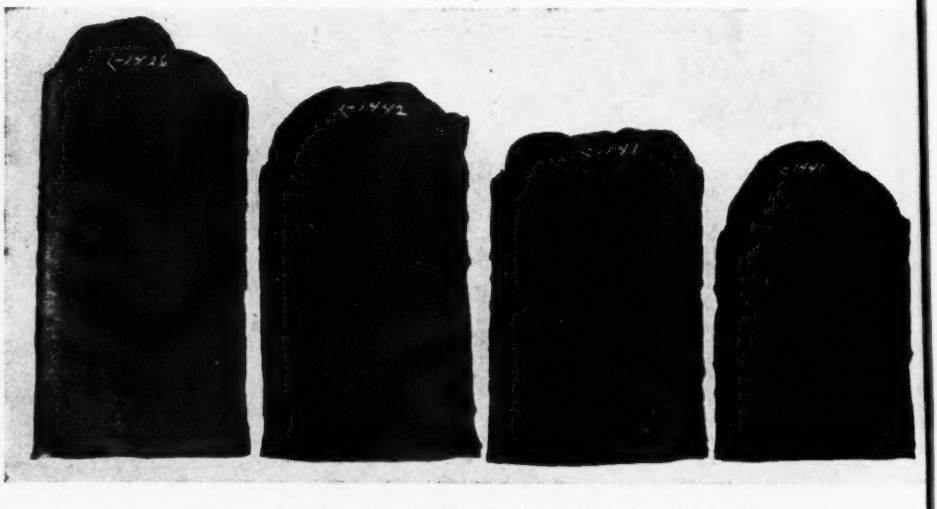

FIG. 5.—Effect of mechanical treatment on length and smoothness of uncured calendered stocks of acetylene black in GR-S.

Fluffy black | Heavy compressed | Ball-milled | Ball-milled and pelletized

gates, were substantially altered by straight-forward mechanical work on the carbon black.

This change in structure tendency is further substantiated by similar experiments with a second commercial carbon, Philblack. Philblack is similar to acetylene black in its smooth-out and high modulus characteristics. Figure 6 shows the effect of mechanical action on length and smoothness of stocks compounded with Philblack. Table V shows that a loss in modulus for Philblack occurred with mechanical processing, although ultimate tensile strength does not change.

In another experiment, a Cabot experimental HMF black, believed to have structure tendency to a lesser degree than acetylene black or Philblack, was

TABLE V

EFFECT OF MECHANICAL TREATMENT ON RUBBER PROPERTIES OF PHILBLACK

Sample	Cure at 292° F (min.)	Modulus 200%	Modulus 300%	Modulus 400%	Ultimate tensile	Elongation (%)	Shore hardness	Hysteresis
Fluffy Philblack	30	750	1410	1940	2250	480	67	..
	60	780	1480	2050	2350	450	69	0.090
	90	820	1580	2150	2240	410	70	..
Ball-milled, pelletized Philblack	30	500	1070	1550	2250	530	66	..
	60	650	1330	1920	2350	490	67	0.095
	90	660	1260	1880	2380	480	68	..

Fluffy black

Ball-milled and pelletized

FIG. 6.—Effect of mechanical treatment on length and smoothness of uncured calendered stocks of Philblack in GR-S.

subjected to mechanical pelletizing action for an extended period. The density was thus increased from 18 to 32 pounds per cubic foot. The effect of the mechanical action in lowering modulus is evident in Figure 7. However, for this material possessing less structure, it was necessary to increase the density to 26 pounds per cubic foot before a significant change in modulus was observed. Tensile strength again remains constant until densities above 30 pounds per cubic foot are attained.

Finally, when an SRF black is subjected to straight mechanical compression (Table VI), no change in modulus properties is noted. It is believed that secondary aggregates in this type of black are so nearly absent that mechanical compression to 29.3 pounds per cubic foot produced no change in rubber properties. However, compression densities of only 18 pounds per cubic foot are sufficient to lower the modulus of a high structure black such as acetylene black. The authors feel, however, that continued mechanical action will eventually produce an effect on SRF black.

TABLE VI

EFFECT OF HEAVY COMPRESSION ON RUBBER PROPERTIES OF SRF BLACK

	Cure at 292° F (min.)	Raw material density, 12.5 (lb. per cu. ft.)	Compressed to density of 29.3 lb. per cu. ft.
Ultimate tensile strength	15	1860	1880
	30	2710	2640
	60	2660	2680
	90	2540	2680
Modulus at 300%	15	700	700
	30	1300	1300
	60	1580	1500
	90	1560	1550
Modulus at 400%	15	1090	1080
	30	1900	1870
	60	2260	2180
	90	2220	2210

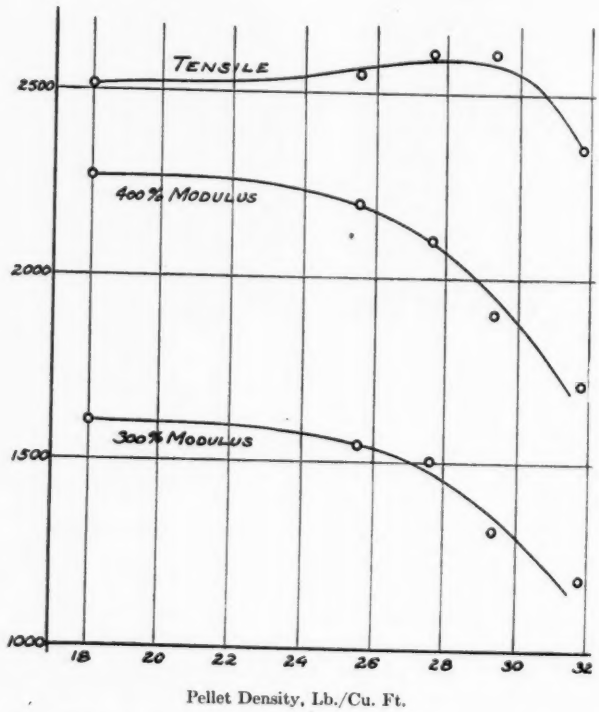

FIG. 7.—Effect of continued mechanical action in pelletization machinery on an experimental HMF black (unpelletized raw material).

CONCLUSIONS

It was suggested that carbon blacks owe some of their characteristic properties to a tendency for individual particles to cluster into chainlike groupings or secondary aggregates.

Results of mechanical processing experiments show that application of mechanical work altered or destroyed secondary aggregates. This conclusion was made since resistance to compression had been permanently overcome.

Analytical measurements confirmed the supposition that secondary aggregates had been altered or destroyed, since oil absorption and liquid retention values markedly decreased with mechanical work.

Finally, properties of compounded GR-S stocks were seriously altered—namely, smoothness of milled stock, high modulus, and enhanced electrical conductivity. It is concluded that these properties were originally caused by the presence of secondary aggregates or structure units.

Alternative interpretations of these data are possible—namely, it might be concluded that it was not possible to disperse the densified material to the same extent as the original carbon black. However, this hypothesis contends that a large particle size material is being dispersed. Therefore, a decrease in tensile strength should have been noted.

There is also some meager evidence suggesting that the chemical nature or activity of the carbon black surface was altered, so that its contribution to modulus was limited. It is believed, however, that most of the evidence offered by the data presented here preponderantly supports the structure theory of high modulus blacks.

The authors consider these results as preliminary in the study of the structure properties of carbon blacks. They appear to be of sufficient interest to be brought to the attention of those studying reinforcement. Data available at present do not permit an interpretation of the contribution of structure to properties of "smooth-out" modulus and electrical conductivity of compounded rubber stocks.

ACKNOWLEDGMENT

The authors acknowledge with thanks the valuable help of collaborators in obtaining these data, particularly R. A. Beebe for his assistance in making heat of adsorption measurements, and W. R. Smith for helpful criticism in preparing the manuscript. We are further indebted to Shawinigan Chemicals Company and Phillips Petroleum Company for permission to use their products.

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DETERMINATION OF POLYSTYRENE IN GR-S RUBBER *

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INTRODUCTION

In the preparation of GR-S and other copolymers by emulsion polymerization, the monomers are usually mixed before they are added to the aqueous solution of soap and catalyst. In the preparation of GR-S, it is essential not to add the styrene to the aqueous solution before the addition of butadiene because styrene polymerizes much more rapidly than butadiene or a mixture of butadiene and styrene. If, in actual plant practice, the styrene is permitted to be in contact with the solution of soap and catalyst before addition of butadiene, the copolymer obtained is not pure GR-S, but a mixture of GR-S and polystyrene.

In the early days of the preparation of GR-S, plant samples of low conversion were often found to have an abnormally high styrene content[1]. It was suspected that the high styrene content was due to the fact that the samples consisted of a mixture of polystyrene and GR-S. A method for the determination of polystyrene in GR-S was, therefore, needed.

In 1943 an approximate method for the determination of polystyrene in GR-S was developed in this laboratory. The method was based on the fact that the addition product of GR-S with iodine monochloride is only slightly soluble in a mixture of 25 per cent of ethanol in benzene, whereas polystyrene is completely soluble. After removal of the precipitated addition product, all the polystyrene and the fraction of the iodine monochloride addition product remaining in solution can be precipitated by the addition of a large quantity of of ethanol. To find the polystyrene content of the weighed precipitate, it is necessary to determine the amount of the iodine monochloride addition product present, which can be done by means of an iodine analysis.

The quantity of addition product that precipitates with the polystyrene depends on the molecular-weight distribution of the former. In other words, when more material of low molecular weight is present, more addition product is not removed in the first precipitation. For this reason the method was found to be satisfactory only for the determination of relatively large amounts of polystyrene (75 per cent) in high-conversion GR-S. It was not suitable for polystyrene determinations in low-conversion GR-S and in high-conversion GR-S containing small amounts of polystyrene.

An attempt was then made to make use of the fact, noted in this laboratory, that the solubility of GR-S in a mixture of benzene and acetone is small, whereas polystyrene is freely soluble in such mixtures. For example, in a mixture of 80 per cent of acetone and 20 per cent of benzene, varying amounts

* Reprinted from the *Journal of Polymer Science*, Vol. 1, No. 5, pages 429–433, October 1946. The investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

of a low-conversion (24 per cent) GR-S sample prepared by bottle polymerization were almost completely separated from high-conversion (80 per cent) polystyrene. To 20 cc. of benzene solutions containing varying ratios of high-conversion polystyrene and low-conversion GR-S in a total concentration of 1 per cent, 80 cc. of acetone was added. The precipitated GR-S polymer was filtered off and was found to contain about 1 per cent of polystyrene (from a determination of the iodine number). The filtrate was then added to a large volume of ethanol to precipitate the remaining copolymer and polystyrene. The amounts of polymer found in this second precipitation are given in Table I.

TABLE I

SEPARATION OF 24 PER CENT-CONVERSION GR-S AND HIGH-CONVERSION POLYSTYRENE IN BENZENE–ACETONE (20:80)

GR-S in original mixture (%)	Polystyrene in original mixture (%)	Polymer not precipitated in 20:80 benzene–acetone (%)
100	0	1.8
		2.0
95	5	5.8
		6.5
75	25	25.5
		24.8
50	50	48.0
		47.8

The results summarized in Table I and those of other experiments have shown, however, that the use of a benzene–acetone mixture is not suitable for the quantitative separation of GR-S from polystyrene. The reason is that GR-S contains low molecular-weight fractions which are soluble in the benzene–acetone mixture. The principle of separation is mentioned here because it allows a fairly close separation of the GR-S from polystyrene without affecting either substance chemically.

The following procedure describes a possible method for the quantitative determination of polystyrene in GR-S based on the above separation Collect quantitatively and weigh the GR-S fraction which precipitates when acetone is added to a benzene solution of the sample. This fraction is practically free of polystyrene. Precipitate the remaining copolymer and polystyrene in the benzene solution by the addition of ethanol, and weigh. From the weight of both precipitates and the unsaturation of both fractions (iodine monochloride method), the polystyrene content of the original sample can be calculated.

This method was abandoned in favor of a much simpler procedure which is described below. In brief, the new method is based on the principle that polymer molecules (such as GR-S) containing ethylenic bonds, when dissolved in benzene, can be broken into fragments by a hydroperoxide in the presence of osmium tetroxide; polymer molecules (such as polystyrene) containing no ethylenic bonds remain unattacked. The small fragments (aldehydes of low molecular weight) are soluble in ethanol, whereas the unattacked polystyrene is insoluble. Separation of the polystyrene, therefore, consists merely of pouring the reaction mixture (after breakdown of the polymer containing unsaturated groups) into ethanol and filtering off the polystyrene.

It is expected that the oxidation of GR-S described in this paper may be of greater importance in connection with a study of the structure of the copolymer. A quantitative determination of all the oxidation products should give a com-

plete insight into the structure of GR-S and other polymers containing unsaturated bonds. The method appears to have definite advantages over degradation by ozone. This problem will be studied further by H. A. Laitinen of the University of Illinois.

In a subsequent paper we shall describe the reactivity of polymers containing unsaturated groups with perbenzoic acid in an organic solvent and also with perbenzoic acid in the presence of a small amount of osmium tetroxide. With perbenzoic acid alone the double bonds form an oxirane ring, *i.e.*, an epoxide, whereas in the presence of osmium tetroxide, oxidation to aldehydes occurs[2]. Several analytical applications of these reactions will be described later.

REAGENTS

tert-Butyl Hydroperoxide.—A mixture containing 60 per cent of *tert*-butyl hydroperoxide and 40 per cent of *tert*-butyl alcohol was obtained from Union Bay State Company, Cambridge, Massachusetts. The mixture is stable for at least several months at room temperature[3].

Osmium Tetroxide Solution.—0.08 g. of osmium tetroxide was dissolved in 100 cc. of reagent-grade benzene. The solution is stable for several months if protected from light. Decomposition is indicated by the formation of a black precipitate, osmium sesquioxide or osmium dioxide.

PROCEDURE

Heat 40–50 g. of *p*-dichlorobenzene contained in a 125-cc. Erlenmeyer flask to 50–60° C. Weigh out a 0.5 to 0.6-g. sample of polymer accurately to 1 mg. and transfer it to the flask. Heat the solution to about 130° C, and maintain the temperature until the sample has dissolved. Even polymers containing gel are dissolved by this procedure. If the sample contains no gel, it dissolves in 15–30 minutes. A hot plate, not an open flame, should be used to heat the solution. If a flame is used, the polymer sticks to the bottom of the flask, due to the high temperature of the glass surface.

Cool the solution to 80–90° C, and add 10 cc. of 60% *tert*-butyl hydroperoxide. Add 1 cc. of 0.003 *M* osmium tetroxide solution in benzene. Heat the solution to 110–115° C, and keep at this temperature for 10 minutes. The solution should be perfectly clear at this point.

Cool the solution to 50–60° C and add 20 cc. of benzene. Pour the solution slowly into 250 cc. of ethanol containing a few drops of concentrated sulfuric acid. Stir the mixture by means of a mechanical stirrer during this addition. Wash the flask with small portions of benzene. Stir the mixture until the polystyrene has coagulated and the solution is clear. If necessary, the solution should be allowed to stand overnight.

Filter the solution through a sintered glass filter[4], which has previously been weighed with an accuracy of 1 mg., and wash with ethanol. Dry the filter at 110° C for 4 hours. Finally cool and weight the filter.

DISCUSSION

The following preliminary experiments led to specifications for the optimum conditions for a routine procedure.

(1) 0.5 g. of GR-S (free of polystyrene impurity) was dissolved in 50 g. of melted *p*-dichlorobenzene. The mixture was cooled to 90° C, and 10 cc. of *tert*-butyl hydroperoxide and 1 cc. of a benzene solution 0.003 *M* in osmium tetroxide were added. The temperature of the solution was maintained at 95–100° C and 1-cc. aliquots were removed from time to time and added to 5 cc. of absolute ethanol. The portions taken after 1, 2, 3, 4, and 5 minutes of heating produced turbidities. The portions taken after 6 or more minutes of heating gave clear solutions when added to the ethanol. To insure a complete breakdown of GR-S in the routine procedure, a temperature of 110–115° C for 10 minutes has been specified.

(2) Similar experiments were made in which varying amounts of osmium tetroxide were used. Because of the fact that osmium tetroxide catalyzes the decomposition of the hydroperoxide and also because of the high price of osmium tetroxide, a higher concentration of the catalyst than is given in the procedure is not recommended. If no osmium tetroxide is added, the breakdown of the GR-S is not apparent even after a long period of heating at 110°.

(3) 0.5 g. of GR-S was treated according to the procedure given in (1). The reaction mixture was poured into 70 per cent ethanol–30 per cent water. A perfectly clear solution resulted, indicating that the aldehyde fragments are small.

(4) Mixtures of GR-S and polystyrene (prepared by emulsion polymerization) were analyzed by the procedure given above. The results are reported in Table II.

TABLE II

DETERMINATION OF POLYSTYRENE IN POLYSTYRENE–GR-S MIXTURES

Polystyrene taken (mg.)	GR-S taken (mg.)	Polystyrene found (mg.)
0	500	0
10	500	9.9
200	300	201.4
500	0	499.0

TABLE III

DETERMINATION OF POLYSTYRENE IN PLANT SAMPLES

Polymer	Conversion (%)	Polystyrene found (%)	
		By osmium tetroxide method	By iodine monochloride method
17 P 35 A 2-b	12	0.3	5
17 P 42 A 1-b	12	2.8	14
Blend B-f	72	0.0	0
17 P 41 A 2-b	16	27.0	33

The procedure has been used for the determination of polystyrene in GR-S samples prepared in the government pilot plant of the University of Akron. In the preparation of samples, the polymerization was started after the addition of styrene, but before the addition of butadiene. As was expected, these samples were found to contain polystyrene. In the preparation of sample "Blend B-f" the charges were prepared in such a way that polymerization of styrene could not occur before the copolymer began to form.

SUMMARY

A convenient procedure for the determination of polystyrene in GR-S is given. The method depends upon degradation of the GR-S by *tert*-butyl hydroperoxide in the presence of a trace of osmium tetroxide. Polystyrene is not attacked and is separated by precipitation with ethanol.

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REPRODUCIBILITY OF TENSILE, PERMANENT SET, AND HARDNESS TEST RESULTS IN THE SAME LABORATORY *

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I. INTRODUCTION

The errors that may arise in determining the tensile properties of vulcanized rubber have been investigated by many workers. It would appear necessary, however, for each laboratory to carry out its own tests to determine the degree of accuracy normally obtained and whether improvement is possible. With this end in view an investigation has been undertaken by the Research Association of British Rubber Manufacturers. The points on which information was sought in the work here described were: (1) the extent of variation to be expected among the results of repeat tensile and permanent set tests made on different days on specimens taken from the same sample of rubber; (2) the effect of the gradual loss of sharpness of the knives used for cutting the specimens; (3) whether ring or dumb-bell specimens give the more consistent results for stress-strain properties; (4) what degree of reproducibility is to be expected in hardness measurements made on different days on the same specimen of rubber, and on different specimens from the same rubber.

It must be noted that variations arising in the mixing and vulcanizing procedures were not considered in this investigation, but only those arising in the preparation of the test-pieces and their testing.

No special precautions were taken in these tests. All the cutting and testing were carried out in the normal manner and by the usual operators, these being in most cases changed from time to time so that the variations observed would include those due to the personal factor.

II. EXPERIMENTAL

(i) MIXING

The two mixes used were:

	A	B
Washed smoked sheet	100	100
Sulfur	3	3
Gas black	—	10
Whiting	—	35
Zinc oxide	5	5
Stearic acid	1	2
Diphenylguanidine	0.75	0.75

These two mixes were chosen to represent respectively a "pure" type and an ordinary loaded type of rubber. It was considered desirable to use both types because it has been found that test-pieces cut from vulcanizates of loaded

* Reprinted from the *Journal of Rubber Research*, Vol. 15, No. 11, pages 215–235, November 1946.

mixes appear to be more uniform and to contain fewer flaws than those prepared from rubbers of the "pure" type.

Two batches of mixing A, each containing 2,000 grams of rubber, were prepared, each divided into halves, and half of each batch blended together, thus giving altogether some 4,400 grams of uniform stock. This was sheeted out 5 mm. thick and used for the preparation of sheets for ring test-pieces. A third batch, containing 2,000 grams of rubber, was prepared, sheeted out 3 mm. thick, and used for making the sheets for dumb-bell specimens.

A similar procedure was adopted for mix B, except that each batch contained 1,700 grams of rubber.

(ii) VULCANIZATION

A special procedure was adopted to minimize errors due to inequalities in degree of vulcanization.

(*a*) *Sheets for Ring Test-Pieces.*—The stock was placed in frame moulds $10 \times 10 \times 0.2$ inches between thin aluminum sheets, each mould being then placed between two 0.1 inch thick iron plates. Four such moulds were placed in the four openings of a 12×12 inch steam-heated platen press kept at 100° C; the press was just closed, but without applying any substantial pressure, and the whole left for 5 minutes. A total hydraulic pressure of 17 tons was then applied to 5 minutes. Twelve filled moulds were prepared in this way, and were stacked, together with their iron plates, in an autoclave press with five $\frac{5}{8} \times \frac{1}{8}$ inch section iron strips inserted between adjacent moulds to act as distance-pieces.

The autoclave was then closed and the ram raised until the pile of moulds just touched the head of the press. The steam pressure was then raised as quickly as possible to 60 lb. per sq. in., which required about 10 minutes, after which a hydraulic pressure of $7\frac{1}{2}$ tons was applied to the ram.

For mix A a stand of 30 minutes at this steam pressure, corresponding to 153° C, was given; for B the stand was 40 minutes. Mixes A and B were moulded and vulcanized separately. The vulcanized sheets were numbered 1 to 12 starting from the bottom of the pile.

(*b*) *Sheets for Dumb-bell Test-Pieces.*—Not enough moulds were available for the vulcanization of all the sheets to be carried out simultaneously as described above, hence a different procedure was adopted. Eight sheets of rubber, each $6 \times 6 \times 0.1$ inches, were vulcanized in moulds between stainless-steel cover plates in an 18×18 inch platen press, four being placed in each of the two "daylights". The sheets were numbered 1 to 4 (top daylight) and 5 to 8 (bottom daylight) in a clockwise direction starting from the back left-hand corner.

From each sheet were cut 4 dumb-bell specimens parallel to the front of the press and to the grain of the sheet. These dumb-bells were numbered in order from back to front, thus: Sheet 1—dumb-bells 1–4; Sheet 2—dumb-bells 5–8; and so on to Sheet 8—dumb-bells 29–32. Two further similar sets of sheets were prepared, giving dumb-bells 33–64 and 65–96, respectively.

(iii) PREPARATION AND TESTING OF SPECIMENS

The vulcanized sheets were conditioned in a room kept at between 60° and 75° F for 12 days before cutting and testing commenced. From rubber A test-pieces were cut daily as required, but from rubber B all the test-pieces

were cut at once and a certain number then tested each day. Tests were carried out each day, usually excluding week-ends, as long as there were enough test-pieces, and the cutting-knives were sharpened at the end of each Saturday morning.

(*a*) *Sheets for Ring Test-Pieces.*—The sheets made for the preparation of ring test-pieces were assumed to be all at the same state of vulcanization, since experience has shown that the autoclave press gives very uniform vulcanization. Accordingly, 8 rings were cut and tested each day from the half of one sheet, using sheet No. 1 for the first two days, No. 2 for the next two days, and so on.

The ring specimens were cut with the standard Schopper knives without lubricant, using a Schopper punch. All rings from rubber A were cut on a cardboard backing, but those from B were cut on a backing of thin sheet gutta-percha. The latter rings, however, were not so cleanly cut as those cut on cardboard, and gave a greater proportion of low values for tensile strength.

The rings were broken on a Schopper tensile testing machine worked by a 0.25 h.p. electric motor, the rate of traverse of the bottom pulley being 16 inches per minute. The mean thickness of each ring was measured by the R.A.B.R.M. thickness gauge[1]. The testing machine was fitted with the special load scale previously described[2], and two observers, for the load and elongation scales respectively, were used.

Permanent set tests were made on the outer rings given by the standard Schopper knives, the internal diameter being 52.6 mm. and the external diameter 57.0 mm. Four rings, from corresponding positions in each day's half-sheet of rubber, were used for each test. The rings were stretched over pulleys to 400 per cent (for A) or 200 per cent (for B) elongation for 15 minutes and then allowed to recover for 60 minutes. The set was then measured by means of the conical gauge previously described[1]. As these tests were made before the investigation[3] which showed the necessity for taking a "zero" measurement on the unstretched ring, this measurement was not taken. The results may, therefore, be affected by errors due to inequality in the initial diameters of the rings. With rubber B, however, the variations due to these errors are probably very small, as all the rings were cut at one time.

Hardness tests on rubber A were made on two discs taken from corresponding positions in each day's half-sheet of rubber. With rubber B the hardness test was repeated daily on the same two discs. Hardness was measured by the R.A.B.R.M. gauge, the results being expressed as the hardness number, *i.e.*, the depth of indentation (mm./100) by a 0.25-inch diameter ball under a load of 1 kilogram acting for 30 seconds. The test-piece consisted of the two superposed discs, 45 mm. in diameter, giving a total thickness of about 10 mm.; with rubber A, where a fresh test-piece was used each day, this thickness varied from 9.7 to 10.5 mm. Two measurements were made on each side of the test-piece and the four results averaged.

(*b*) *Sheets for Dumb-bell Test-Pieces.*—With the sheets prepared for dumb-bell specimens there was considered to be more probability of variation in state of vulcanization, owing to the sheets having been made in three lots. The test-pieces for each day's tests were therefore selected as follows so as to minimize the effects of any such variation (this is not a random arrangement, but was designed to make the average properties of each day's set of dumb-bells as nearly as possible the same):

	Dumb-bells Nos.:							Dumb-bells Nos. :					
1st day	1	29	33	61	65	93	9th day	9	21	41	53	73	85
2nd day	2	30	34	62	66	94	10th day	10	22	42	54	74	86
3rd day	3	31	35	63	67	95	11th day	11	23	43	55	75	87
4th day	4	32	36	64	68	96	12th day	12	24	44	56	76	88
5th day	5	25	37	57	69	89	13th day	13	17	45	49	77	81
6th day	6	26	38	58	70	90	14th day	14	18	46	50	78	82
7th day	7	27	39	59	71	91	15th day	15	19	47	51	79	83
8th day	8	28	40	60	72	92	16th day	16	20	48	52	80	84

Dumb-bell specimens, of a shape described by Dawson and Porritt[4], were cut by a die fitted into the Schopper punch. All cutting was done on a cardboard backing. No lubricant was used in cutting the dumb-bells.

The specimens were broken on a Scott tensile testing machine driven by a $\frac{1}{6}$ h.p. motor, the lower grip moving at 20 inches per minute. The thickness of each dumb-bell was measured by a Mercer dial micrometer gauge exerting a pressure of 180 g. per sq. cm. on the rubber. The 1-inch test length was marked by a 2-bladed die. Elongations during the test were measured by a scale, graduated in tenths of an inch, held alongside the specimen.

Hardness tests on rubber A were made on two dumb-bells from the middle of each day's set, *i.e.*, those in the middle two columns of the distribution table shown above. For rubber B the hardness test was repeated daily on the same two pieces cut from one of the vulcanized sheets; these pieces measured about 32 mm. square, and were thus of roughly the same size as the widened ends of the dumb-bells on which the tests were made in the case of rubber A. The thickness of rubber tested was about 5 mm., the range of variation in the case of A being 4.8 to 5.2 mm. The hardness measurements were made in the manner described above, paragraph (*a*).

(iv) RESULTS

The results of the tensile tests are given in Tables 1–4, and the hardness and permanent set test results in Tables 5 and 6, respectively. The temperatures quoted are those at which the tests were made. In the tensile test results, except where otherwise stated, each figure is the mean for the 8 rings or 6 dumb-bells, after excluding breaking figures for any obviously faulty specimens. As it has for some years been usual in the R.A.B.R.M. Laboratories to test 4 tensile specimens and take the mean of the highest two tensile strength figures (conveniently termed the 2/4 mean), the values that would most probably have been obtained by applying this method to sets of 4 specimens, picked at random from the 8 or 6 actually used, have been calculated approximately, and are termed *corrected averages.*

The following abbreviations are used for the tensile properties:

TS = average tensile strength (kg. per sq. cm.) of all specimens, excepting obviously faulty ones.
TSC = corrected average tensile strength (kg. per sq. cm.) as defined above.
EB = elongation at break (percentage).
E25 (50, 75, 100) = elongation (percentage) at 25 (50, 75, 100) kg. per sq. cm.
M100 (300, 500, 700) = modulus (kg. per sq. cm.) at 100 (300, 500, 700)% elongation.

TABLE 1

RUBBER A, RING SPECIMENS CUT ON DAY OF TEST

Date			Temperature (° F)	TS	TSC	E25	E50	E75	E100	EB
Tues.	Feb.	11	66	170	176	408	546	606	649	734
Wed.	Feb.	12	64	165	175	405	545	607	649	729
Thurs.	Feb.	13	64	158	163	399	537	597	639	710
Fri.	Feb.	14	66	156	164	406	544	605	645	715
Mon.	Feb.	17	68	157	171	408	547	607	649	716
Tues.	Feb.	18	66	163	177	420	550	607	648	724
Wed.	Feb.	19	65	168	177	410	543	602	641	721
Thurs.	Feb.	20	64	159	168	406	542	601	643	716
Fri.	Feb.	21	68	170	177	411	543	603	644	730
Mon.	Feb.	24	63	169	176	419	549	607	650	731
Tues.	Feb.	25	63	182	185	412	546	604	647	748
Wed.	Feb.	26	63	144	176	409	544	603	645	701
Thurs.	Feb.	27	66	149	165	406	545	604	646	709
Fri.	Feb.	28	67	174	179	410	546	604	647	740
Mon.	March	2	62	160	166	411	544	603	644	715
Tues.	March	3	62	169	175	409	542	601	642	728
Wed.	March	4	62	166	167	409	542	599	642	723
Thurs.	March	5	66	167	172	414	548	608	648	731
Fri.	March	6	67	162	166	406	542	602	644	722
Sat.	March	7	66	160	167	412	550	609	652	726

TABLE 2

RUBBER B, RING SPECIMENS ALL CUT ON SAME DAY

Date			Temperature (° F)	TS	TSC	E25	E50	E75	E100	EB
Tues.	Feb.	11	66	159	177	(a)	(a)	(a)	(a)	585
Wed.	Feb.	12	66	167	177	213	358	433	487	596
Thurs.	Feb.	13	65	180	188	218	361	434	488	612
Fri.	Feb.	14	64	181	192	210	351	423	477	606
Mon.	Feb.	17	66	178	185	210	353	428	483	603
Tues.	Feb.	18	65	163	170	209	349	422	476	579
Wed.	Feb.	19	70	162	172	215	361	437	491	593
Thurs.	Feb.	20	65	170	187	206	347	422	474	584
Fri.	Feb.	21	67	174	185	205	346	419	472	587
Mon.	Feb.	24	62	173	181	206	349	425	479	595
Tues.	Feb.	25	63	188	198	203	344	417	469	604
Wed.	Feb.	26	63	173	179	212	352	427	481	598
Thurs.	Feb.	27	63	166	184	200	345	418	475	583
Fri.	Feb.	28	66	156	175	207	349	424	478	572
Mon.	March	2	60	183	186	204	343	416	471	603
Tues.	March	3	60	165	188	203	342	418	470	574
Wed.	March	4	62	157	171	204	343	416	467	555

(a) Readings accidentally omitted.

TABLE 3

RUBBER A, DUMB-BELL SPECIMENTS CUT ON DAY OF TEST

Date			Temperature (° F)	TS	TSC	M100	M300	M500	M700	EB
Wed.	Feb.	12	69	252	274	7.9	21.4	63.8	—	707
Thurs.	Feb.	13	66	258	275	7.8	21.6	63.6	251	712
Fri.	Feb.	14	66	254	264	7.9	21.2	63.1	249	708
Mon.	Feb.	17	64	266	279	7.0	20.5	60.9	256	709
Tues.	Feb.	18	67	253	266	8.2	22.0	61.0	—	700
Wed.	Feb.	19	69	269	281	7.7	21.6	60.1	250	717
Thurs.	Feb.	20	65	263	276	7.2	20.2	60.5	248	708
Fri.	Feb.	21	61	268	278	8.0	22.0	60.6	258	713
Mon.	Feb.	24	64	256	278	7.6	21.5	62.5	—	698
Tues.	Feb.	25	63	269	280	7.6	21.5	62.2	265	704
Wed.	Feb.	26	69	259	272	7.0	20.4	62.9	—	691
Thurs.	Feb.	27	67	263	273	7.8	21.4	63.2	258	704
Fri.	Feb.	28	69	268	281	6.8	20.7	64.0	—	698
Mon.	March	2	65	265	284	6.5	20.4	63.0	256	703
Tues.	March	3	63	264	283	7.1	21.0	63.3	257	705
Wed.	March	4	62	260	281	7.2	21.1	64.1	—	690

TABLE 4

RUBBER B, DUMB-BELL SPECIMENS ALL CUT ON SAME DAY

Date			Temperature (° F)	TS	TSC	M100	M300	M500	EB
Wed.	Feb.	12	68	235	239	16.6	52.4	167	578
Thurs.	Feb.	13	67	242	250	15.8	52.8	169	585
Fri.	Feb.	14	67	233	238	14.7	50.6	164	582
Mon.	Feb.	17	66	235	240	16.3	54.0	165	582
Tues.	Feb.	18	67	224	234	15.8	53.4	160	581
Wed.	Feb.	19	68	235	242	15.7	52.9	161	589
Thurs.	Feb.	20	66	236	244	15.6	55.5	162	583
Fri.	Feb.	21	66	229	248	16.8	55.4	167	570
Mon.	Feb.	24	64	230	248	16.2	56.6	173	563
Tues.	Feb.	25	63	240	254	18.0	59.0	178	573
Wed.	Feb.	26	60	229	240	16.0	56.6	171	567
Thurs.	Feb.	27	67	237	242	16.8	56.8	173	573
Fri.	Feb.	28	62	243	245	15.1	56.2	176	576
Mon.	March	2	66	229	235	16.1	55.4	165	577
Tues.	March	3	64	231	237	17.5	56.5	170	582
Wed.	March	4	62	232	236	17.8	57.6	172	587

TABLE 5

HARDNESS NUMBER (H)

Date			A, ring		B, ring		A, dumb-bell		B, dumb-bell	
			Temp. (° F)	H	Temp. (° F)	H	Temp. (° F)	H	Temp. (° F)	H
Tues	Feb.	11	66	143	66	95	—	—	—	—
Wed.	Feb.	12	66	138	66	94	69	116	69	80
Thurs.	Feb.	13	66	137	66	94	66	114	66	80
Fri.	Feb.	14	61	138	61	95	61	115	61	83
Mon.	Feb.	17	63	138	63	96	66	115	66	82
Tues.	Feb.	18	66	136	66	96	66	114	66	81
Wed.	Feb.	19	65	136	68	92	68	113	68	80
Thurs.	Feb.	20	65	135	65	95	65	114	65	80
Fri.	Feb.	21	65	140	65	95	65	113	65	80
Mon.	Feb.	24	62	139	62	94	62	112	62	78
Tues.	Feb.	25	63	138	63	92	63	111	63	78
Wed.	Feb.	26	65	138	65	94	65	110	65	77
Thurs.	Feb.	27	64	139	64	92	63	115	63	80
Fri.	Feb.	28	66	139	66	91	65	110	65	79
Mon.	March	2	61	141	61	93	62	111	62	78
Tues.	March	3	64	139	64	94	64	114	64	80
Wed.	March	4	62	138	62	92	62	113	62	80
Thurs.	March	5	63	141	63	94	—	—	63	81
Fri.	March	6	65	138	—	—	—	—	—	—
Sat.	March	7	67	140	—	—	—	—	—	—

TABLE 6

PERMANENT SET OF RING SPECIMENS

Date			Temperature (° F)	Permanent set (%)	
				A	B
Tues.	Feb.	11	66	2.9	4.5
Wed.	Feb.	12	68	3.0	4.3
Thurs.	Feb.	13	66	3.0	4.8
Fri.	Feb.	14	66	3.25	4.75
Mon.	Feb.	16	66	3.0	5.25
Tues.	Feb.	18	66	3.05	4.55
Wed.	Feb.	19	67	3.1	4.3
Thurs.	Feb.	20	65	3.1	4.4
Fri.	Feb.	21	69	3.15	4.6
Mon.	Feb.	24	60	3.1	4.25
Tues.	Feb.	25	64	3.4	4.3
Wed.	Feb.	26	67	3.1	4.6
Thurs.	Feb.	27	69	3.3	4.2
Fri.	Feb.	28	66	3.0	4.35
Mon.	March	2	61	3.3	4.75
Tues.	March	3	65	3.45	4.3
Wed.	March	4	62	3.1	4.5
Thurs.	March	5	65	3.3	4.6
Fri.	March	6	68	2.85	—
Sat.	March	8	68	3.2	—

(v) CORRECTIONS FOR AGING, BLUNTING OF KNIVES, AND TEMPERATURE

Before attempting to consider the degree of reproducibility obtainable in tensile, hardness, and permanent set tests, it is necessary to determine whether the results are influenced by extraneous factors such as the aging of the rubber, gradual blunting of the cutting knives (in the case of tensile-test specimens cut on the day of test), and variations in test temperature. If such influences appear to be appreciable, corrections for them must be applied to the results.

(*a*) *Blunting of Knives.*—It is known[5], that blunting of the knives used for cutting tensile-test specimens may considerably reduce their tensile strength. Since, in the present investigation, the knives were sharpened at the end of each Saturday morning, the tensile strength must tend to fall during each week. It is therefore necessary to estimate the magnitude of this effect and allow for it. This can be done by averaging all the results on the same day of the week. These averages are given in Table 7, the figure in brackets being the number of results in the average.

TABLE 7

	A, rings				A, dumb-bells			
	TS	TSC	EB		TS	TSC	EB	
Mon.	162	171	721	(2)	261	280	703	(3)
Tues.	171	178	733	(4)	262	276	703	(3)
Wed.	161	174	718	(4)	259	276	705	(4)
Thurs.	158	167	716	(4)	261	275	708	(3)
Fri.	166	172	727	(4)	263	274	706	(3)
Sat.	160	167	726	(1)	—	—	—	—

These results show that in most cases the tensile strength appears to fall during the week, the approximate average fall per day being as follows: Rings, TS, 1.4 kg. per sq. cm.; TSC, 1.6 kg. per sq. cm.; Dumb-bells, TS, 0; TSC, 1.1 kg. per sq. cm.

As the average test temperature shows no progressive change between Monday and Saturday, and the effect of aging is, if anything, to increase the tensile strength, the observed decrease may be attributed to the blunting of the knives. Corrections based on the rates of change noted above have, therefore, been applied to the tensile strength results for rubber A.

(NOTE.—These apparent changes do not prove the existence of a real blunting effect, because the figures from which they are derived (Table 7) possess a relatively large standard error. Thus, there is 1 chance in 20 that the true mean for any day of the week may deviate from the value given in Table 7 by more than the following amount (only an average figure for the 6 days of the week has been given, for the sake of simplicity): Rings, TS, ± 8 kg. per sq. cm.; TSC, ± 6 kg. per sq. cm.; Dumb-bells, TS, ± 6 kg. per sq. cm.; TSC, ± 2 kg. per sq. cm. In a statistical sense, indeed, none of the observed figures for the rate of fall in tensile strength with blunting differs significantly from zero. This, however, in no way invalidates their use for correcting the results for blunting effect, because the observed figures, whether significantly different from zero or not, are the most probable values of this effect so far as can be deduced from the data available, and are therefore the values to be used in making the necessary corrections.)

No significant change in elongation at break is evident in Table 7. The figures for elongation at constant load and rigidity for rubber A were examined similarly, since it appeared possible that blunting of the knives might slightly

alter the width of the specimens, which was assumed to be constant. With the ring specimens the Monday, Tuesday, and Saturday values for elongation are some 3–5 per cent higher than the rest, but there is no progressive change. With the dumb-bell specimens the rigidities remain substantially constant from Monday to Saturday. No corrections for blunting have been applied to these properties.

As blunting might affect also the initial diameter of the permanent set rings, the average permanent set for each day of the week has been determined.

	A, rings	
Mon.	3.15	(3 results)
Tues.	3.2	(4 results)
Wed.	3.1	(4 results)
Thurs.	3.2	(4 results)
Fri.	3.05	(4 results)
Sat.	3.2	(1 result)

There is no evidence of progressive change in the measured set between Monday and Saturday.

(*b*) *Aging.*—The results, corrected where necessary for the effect of blunting as noted above, were examined for aging effects by averaging results obtained in each week. As, however, the weekly average test temperature differed appreciably from week to week, the few results obtained at unusually high or low temperatures were omitted, so as to obtain, for each week, an average for tests made at approximately the same average temperature (within $\pm 1°$ F).

The results so obtained showed in some cases definite signs of progressive change from week to week, these being noted in Table 8. In all other cases the aging effects, if they existed at all, were too small to be detectable with certainty among the variations due to other causes.

The increases in tensile strength for rubber A correspond to 0.4 per cent (rings) and 0.75 per cent (dumb-bells) of the actual tensile strength. Since the percentage increase on aging should be the same for both rings and dumb-bells, an average figure of 0.6 per cent has been used in calculating the corrections.

Corrections based on the aging changes indicated above have been applied to the properties shown in Table 8.

TABLE 8

EFFECTS OF AGING

Property	Change per week
A, rings, tensile strength*	+0.7 kg. per sq. cm.
A, dumb-bells, tensile strength*	+2.0 kg. per sq. cm.
B, rings, elongations at constant loads	−4%†
B, dumb-bells, moduli	+0.027 × modulus
B, rings, breaking elongation	−4% approx.
B, dumb-bells, breaking elongation	−4% approx.

* Mean of TS and TSC; these have been averaged because there is no reason to suppose that they would be differently affected by aging.

† Approximately the same for elongations ot 25, 50, 75, and 100 kg. per sq. cm.

As in the case of blunting, the figures in Table 8 cannot be taken as definite proof of an aging effect, except for the elongations at constant loads and moduli (at 300 and 500 per cent) of the B mix, where a statistical test shows a significant

effect of aging. It is nevertheless legitimate to apply the correction in all cases, for the reason explained in connection with blunting (paragraph (*a*) above).

(*c*) *Temperature.*—After being corrected, where necessary, for blunting of the knives and aging, the results were next plotted against the test temperature. In several cases there appeared to be a change with temperature. These cases are summarized in Table 9.

TABLE 9

EFFECT OF TEMPERATURE

Property	Change for 10° F rise
A, rings, tensile strength*	+3 kg. per sq. cm.
A, dumb-bells, tensile strength*	−6.5 kg. per sq. cm.
B, rings, tensile strength*	−9.8 kg. per sq. cm.
B, dumb-bells, tensile strength*	−4.3 kg. per sq. cm.
B, rings, elongation at constant load†	+6%
B, dumb-bells, modulus	−0.03 × modulus
B, rings, breaking elongation	−5 per cent
B, dumb-bells, breaking elongation	+2 per cent

* Mean of TS and TSC.
† Approximately the same for elongations at 25, 50, 75, and 100 kg. per sq. cm.

It is very unlikely that temperature really has opposite effects on the ring and dumb-bell values for the tensile strength of A, and if an average of the two observed figures is used to estimate the temperature correction, this is found to be always less than 1 kg. per sq. cm. For these reasons it was not considered necessary to apply a temperature correction in this case. For the same reasons no correction has been applied to the breaking elongation of rubber B. In the remaining cases the observed effect is probably not statistically significant (an exact test was not made), but the corresponding corrections have been applied because the temperature effects seem more real and are larger.

The values of the temperature effect for tensile strength of rings and dumb-bells of rubber B correspond to 5.5 and 2 per cent, respectively, of the actual tensile strength; an average value of 4 per cent has therefore been adopted in calculating the corrections.

There were doubtful indications of an increase in breaking elongation and elongations at constant loads with increase of temperature for the rings of rubber A, but as the dumb-bells of this rubber showed no corresponding effects, no corrections have been applied.

By applying the corrections indicated above for blunting of the knives, aging, and temperature variations, values have been obtained to represent the properties of the rubbers at the beginning of the series of tests, using samples cut with freshly sharpened knives and tested at 65° F. These results, where different from those given in Tables 1–6, are given in Tables 10 and 11.

III. DISCUSSION OF RESULTS

(i) TENSILE STRENGTH

The daily means given in Tables 10 and 11 have been used to calculate the figures in Table 12 for the mean value in each complete series of tests (*series mean*) and for the standard error (S.E.) of the daily means, *i.e.*, the root mean square of the deviations of individual means from the series mean. (NOTE.—

TABLE 10

RING SPECIMENS (CF. TABLES 1 AND 2)

Date	A		B						
	TS	TSC	TS	TSC	E25	E50	E75	E100	EB
Feb. 11	172	178	160	178	(a)	(a)	(a)	(a)	558
Feb. 12	168	178	168	178	213	357	433	487	597
Feb. 13	162	167	180	188	220	362	436	490	613
Feb. 14	162	170	180	191	213	354	426	480	607
Feb. 17	156	170	179	186	213	356	431	486	606
Feb. 18	163	178	163	170	213	353	426	480	583
Feb. 19	170	179	165	175	218	363	439	492	597
Feb. 20	162	172	170	187	212	353	428	480	589
Feb. 21	175	182	175	186	210	351	424	477	593
Feb. 24	167	174	171	179	216	359	435	489	602
Feb. 25	182	185	187	197	213	354	427	479	612
Feb. 26	145	177	172	178	222	362	437	491	606
Feb. 27	151	167	165	183	211	356	429	486	592
Feb. 28	178	183	157	176	216	358	433	487	582
Mar. 2	159	163	180	182	217	357	430	486	614
Mar. 3	168	174	162	184	217	357	433	486	586
Mar. 4	166	167	155	169	218	357	430	481	567
Mar. 5	169	174	—	—	—	—	—	—	—
Mar. 6	165	169	—	—	—	—	—	—	—
Mar. 7	164	171	—	—	—	—	—	—	—

(a) Readings accidentally omitted.

TABLE 11

DUMB-BELL SPECIMENS (CF. TABLES 3 AND 4)

Date	A		B					
	TS	TSC	TS	TSC	M100	M300	M500	EB
Feb. 12	252	276	238	242	16.7	52.9	168	578
Feb. 13	258	279	244	252	15.8	52.9	169	586
Feb. 14	254	268	235	240	14.6	50.5	163	584
Feb. 17	265	278	236	241	16.0	53.2	162	585
Feb. 18	252	266	226	236	15.5	52.5	157	585
Feb. 19	267	281	238	245	15.4	52.0	158	593
Feb. 20	261	277	237	245	15.1	54.1	157	588
Feb. 21	266	280	230	249	16.2	53.8	161	576
Feb. 24	253	275	229	247	15.5	54.0	166	570
Feb. 25	266	278	238	252	17.1	56.1	169	581
Feb. 26	256	271	224	235	14.9	53.0	160	575
Feb. 27	260	273	239	244	16.0	54.1	165	582
Feb. 28	264	281	240	242	14.0	52.5	164	586
Mar. 2	261	280	230	236	15.0	51.8	154	587
Mar. 3	259	279	230	236	16.3	52.3	158	593
Mar. 4	255	278	229	233	16.4	52.9	158	599

This is called the *observed standard error* to distingush it from another quantity to be considered later.)

It must be noted that each day's TSC value is the average of all the possible 2/4 means, *i.e.*, means each of the highest 2 values out of 4, obtainable by picking sets of 4 specimens out of the 8 or 6 actually used, so that the standard error

TABLE 12

TENSILE STRENGTH

		A, rings	B, rings	A, dumb-bells	B, dumb-bells
Daily means (TS)	Series mean, kg. per sq. cm.	165.2	170.0	259.0	234.0
	Observed S.E., kg. per sq. cm.	8.9	9.6	5.3	5.7
	Observed S.E. (%)	5.4	5.6	2.0	2.4
Daily means (TSC)	Series mean, kg. per sq. cm.	173.9	181.7	276.2	242.2
	Observed S.E., kg. per sq. cm.	6.0	7.3	4.6	5.8
	Observed S.E., (%)	3.4	4.0	1.7	2.4
2/4 means	Observed S.E., kg. per sq. cm.	{7.4 {8.5	{9.9 {8.2	7.8	6.7
	Observed S.E., (%)	4.6*	5.0*	2.8	2.8

* Mean of results for first and second groups.

of the TSC value is less than that of a single 2/4 mean. The standard error of the latter has, therefore, been deduced from results for sets of 4 specimens chosen from the 8 (or 6) used in each day's tests in the following way: (1) in the case of ring specimens the 8 results were divided into first and second groups of four, separate values of standard error being calculated for the first and second groups; (2) in the case of dumb-bells, where 6 specimens were tested, a group of 4 has been selected by a method varying systematically through the series. Results so obtained are included in Table 12. They serve to show the degree of variation among means obtained by averaging the highest two out of four results, the procedure that has been used for some years in the R.A.B.R.M. Laboratories.

Eliminating the lowest two out of four results, as in calculating the TSC values, leads to series means higher by from 4 to 6.5 per cent than the means including all the results (TS figures). It also usually makes the daily means less variable, as shown by the smaller standard errors of TSC as compared with those of TS.

With both rubbers the dumb-bell specimens give more uniform results, as indicated by the smaller standard errors, than the ring specimens. Too much importance should not be attached to this difference, however, because other factors (method of cutting and distribution of specimens among the different days' tests) were varied at the same time as the form of the test-piece.

The frequency distribution of the deviations of the daily means from the series mean is shown in Figures 1 and 2 for the TS and TSC values, respectively. The results for all four series of tests have been included in each diagram to obtain sufficient values to give an informative distribution curve. The curve shown by a full line is that which best fits the data. In neither case does the observed distribution deviate significantly from a normal probability curve (the broken line in Figure 1 is a normal curve fitted to the data). There is, however, some indication of a slight excess of very low values in the case of TS results, which is eliminated by the TSC method of calculation.

An important point to be considered in connection with the daily means is the source of their variation. Since the results for specimens tested on any one day vary among themselves, their mean is only an estimate of the true value. Hence the means obtained on different days will themselves vary about the true value. The variability among one day's individual results, which may arise from nonuniformity of the material tested and (or) from imperfections in

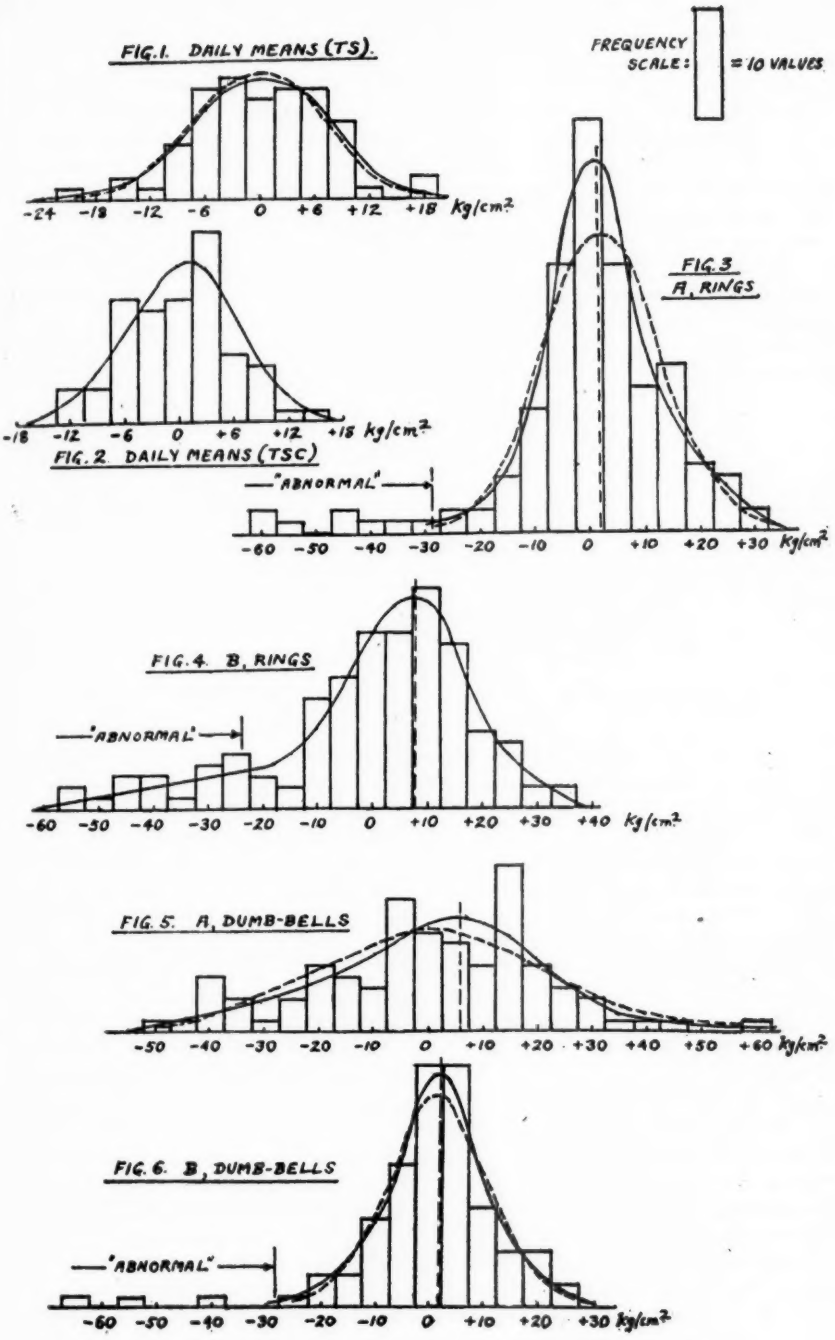
FIG. 1. DAILY MEANS (TS).
FREQUENCY SCALE: = 10 VALUES
-24 -18 -12 -6 0 +6 +12 +18 Kg/cm²
FIG. 2. DAILY MEANS (TSC)
-18 -12 -6 0 +6 +12 +18 kg/cm²
FIG. 3 A, RINGS
"ABNORMAL"
-60 -50 -40 -30 -20 -10 0 +10 +20 +30 Kg/cm²
FIG. 4. B, RINGS
"ABNORMAL"
-60 -50 -40 -30 -20 -10 0 +10 +20 +30 +40 Kg/cm²
FIG. 5. A, DUMB-BELLS
-50 -40 -30 -20 -10 0 +10 +20 +30 +40 +50 +60 kg/cm²
FIG. 6. B, DUMB-BELLS
"ABNORMAL"
-60 -50 -40 -30 -20 -10 0 +10 +20 +30 kg/cm²

the technique of preparing and testing the specimens, will therefore be one cause of variations among the daily means. There are also certain conditions which change from day to day, and although the more obvious of these, namely, temperature, age of rubber, and changes in sharpness of the cutting knives, have been as far as possible allowed for, there may be others unaccounted for which add to the variability of the daily means. It is possible by examining the results to determine the maximum amount of the observed variability of these means that can be accounted for by the variability among results for individual specimens tested on one day, and hence the extent to which these unsuspected variable conditions are operative.

The standard deviation (S.D.) of the individual results, which is strictly the root mean square of their deviations from the daily mean, has been calculated approximately by the convenient *mean range* method, using the average value of the difference between the highest and lowest figure in each day's set[6]. The results so obtained are given in the upper half of Table 13.

TABLE 13

		A, rings	B, rings	A, dumb-bells	B, dumb-bells
Complete results	S.D. of individual results	15	17	23	13
	Average value of n	7.7	7.7	6.0	6.0
	Calculated S.E. of daily means	5.4	6.3	9.5	5.2
	Observed S.E. of daily means*	8.9	9.6	5.3	5.7
Normal results	S.D. of individual results	10	13	—	9.5
	Average value of n	7.3	6.6	—	5.7
	Calculated S.E. of daily means	3.8	5.0	—	4.0
	Observed S.E. of daily means	5.2	7.5	—	6.4

All figures except n are in kg. per sq. cm.
* From Table 12.

The mean range method of calculating standard deviations is not strictly accurate unless the individual values under consideration are distributed according to the normal probability law, which is not quite the case with the present results, as will be shown later. The accuracy was accordingly checked in some cases by calculating the standard deviation by the usual root mean square method. As the two methods always gave results agreeing to within 5 per cent or less, it was concluded that the mean range method is sufficiently accurate for the present purpose.

When several means are obtained, each comprising a certain number (n) of individual values taken at random from a large number, these means are subject to a standard error, which is in effect their standard deviation from the mean of all the results. This standard error is $1/\sqrt{n}$ times the standard deviation of the individual results. Hence, knowing the standard deviation and the value of n (in the present case, the number of specimens tested per day), we can calculate the standard error which the daily means should show if their variability were due entirely to the variability among individual results obtained on any one day; this error is given in the upper part of Table 13 as "calculated S.E. of daily means." The figures in the lower half of the Table are discussed later.

Before discussing the standard errors, it may be noted that the standard deviations of individual results in the four series of tests are respectively 9, 10, 9, and 5.5 per cent of the mean tensile strength. Of these figures the first and last are probably the most indicative of the variation likely to be encountered

in normal practice, since the second figure (B, rings) is probably high owing to the use of gutta-percha backing in cutting the rings, which was found not to give such cleanly cut rings as the usual cardboard, while the third figure (A, dumb-bells) is shown below to be abnormally high, apparently owing to non-uniformity in the material tested. The figures of 9 per cent for A rings and 5.5 per cent for B dumb-bells may be compared with the figures quoted in or deducible from published papers, namely, 8.8, 5.7, 7.5, and 8.3 per cent[7] and 16 per cent[8] for rings, and 6.5 per cent[9] for dumb-bells; Davies and Horrobin[10] obtained a value of 9 kg. per sq. cm. for Schopper rings, this being substantially independent of the actual tensile strength.

The observed standard error of the daily means differs from the calculated value in every case. To determine whether the difference is statistically significant, use has been made of the *variance ratio* or F test[11], in which the square (F) of the ratio of the greater to the smaller standard error is compared with tabulated values of F for various degrees of probability. The results of this test are as follows:

	Values of F			
	A	B	A	B
Experimental (from Table 13)	2.72	2.30	3.24	1.21
Value of 5% probability	1.67	1.72	2.15	1.80
Value for 1% probability	2.04	2.15	3.00	2.28

The fact that the experimental values of F for both sets of rings and for the A dumb-bells exceed the 1 per cent probability values means that in these cases the odds are more than 100 to 1 against the difference between observed and calculated errors being due to chance. That is, the difference is almost certainly real. With the B dumb-bells, however, the odds are much less than 20 to 1, so that a real difference cannot be claimed with any confidence.

There is thus clear evidence that the daily means for ring specimens are more variable than would be expected from the variation observed within test results obtained on the same day. The daily means must therefore be affected by some factor or factors, other than age of the rubber, temperature, and the blunting of the cutting knives, which vary from day to day; the possible nature of these factors is discussed in paragraph (vi) below. It appears, nevertheless, that a considerable part of the variation between daily means is attributable to the variation among results obtained on the same day.

With the dumb-bells of rubber A the daily means are significantly less variable than would be expected from the standard deviation of the individual results. This apparent anomaly could arise from a difference between the sheets of rubber from which the specimens for each day's tests were taken. Thus, if there are, say, 6 sheets for each uniform in itself but differing from the others, groups of 6 specimens, one from each sheet, will show variation within themselves, *i.e.*, a finite standard deviation, and yet the average for each group will be the same, *i.e.*, the standard error of the means will be zero. The existence of such a variation in the material tested can, therefore, give rise to a result similar to that observed.

The results obtained with the A dumb-bells thus incidentally illustrate the disadvantage of distributing specimens among the different days' tests by the method here used, since it may, as in the present case, render it impossible to determine by statistical examination whether or not there are causes of excess day-to-day variation. A random distribution would have been preferable in this case.

It remains to consider the frequency distribution of the individual tensile strength figures. The deviation of each figure from the corresponding daily mean has accordingly been determined and a frequency distribution diagram of these deviations plotted for each of the four series of tests (Figures 3–6).

In Figures 3, 4, and 6 the bulk of the values are distributed according to a substantially symmetrical curve of approximately the normal probability type (normal curves, shown in broken lines, are fitted in some cases), but in each case there is a tail of abnormally low values. In Figure 5 there is no tail, the curve falling to zero at about the same plus and minus deviations from the peak or model value. The curve, however, is unsymmetrical, showing an excess of low values.

The low values, particularly those forming the tails in Figures 3, 4, and 6, may be unreliable figures due to faults preëxisting in the material or produced in preparing the test-pieces. The fact that in Figures 3, 4, and 6 the remainder of the values form a substantially symmetrical diagram may be regarded as supporting, though not proving, this view. It might, indeed, be considered that these low values should have been rejected at the outset, before examining and correcting the results for the effects of temperature variation, aging, and blunting of the knives. This, however, would be tantamount to assuming that the tensile strength values should be distributed according to the normal probability law. There is no justification for such an assumption, since it cannot be tacitly assumed that such low values are not a characteristic property of rubber. In view of the impossibility of deciding from the present results whether these low values are or are not a characteristic of the rubber, it was considered desirable to reëxamine the data after excluding these low results, that is, confining attention to those values forming the normal part of the frequency-distribution diagram. In the case represented in Figure 5 there is no obvious way of deciding which are abnormal values, but in the other cases it was decided to reject all values that fall below the mode (indicated by the vertical broken line) by more than the difference between the latter and the value where the curve falls to zero on the high side. This procedure excludes 8 values out of 154 for A rings, 18 out of 154 for B rings, and 3 out of 96 for B dumb-bells. These are indicated as abnormal in the Figures.

The standard deviation of the remaining normal results, calculated by the mean range method, is shown in the lower half of Table 13, together with the standard error of the daily means calculated from it. In calculating the observed standard error of the daily means, for which the root mean square method was used, it was first necessary to correct some of these means for the exclusion of the abnormal low results. The corrected values so obtained for tensile strength and also breaking elongation are given in Table 14 (these are corrected also for aging, test temperature, and blunting of the knives, where necessary).

As would be expected, the normal results (lower half of Table 13) generally give smaller standard deviations and standard errors than the complete results (upper half). Again, however, the observed standard error in the three cases examined is significantly higher than the value calculated from the standard deviation of individual results. Thus, the value of F for the A rings (1.88) shows that the odds are more than 20 to 1 against the difference between the observed and calculated errors being due to chance, while in the case of the B rings (F = 2.25) and B dumb-bells (F = 2.56) the odds are more than 100 to 1. It may therefore be said that the exclusion of the abnormal results leaves unchanged the conclusion that a part, though not all, of the variation among the

TABLE 14

DAILY MEANS OF TENSILE STRENGTH AND BREAKING ELONGATION, EXCLUDING ABNORMAL LOW RESULTS

A, rings				B, rings				B, dumb-bells			
Date	N	TS	EB	Date	N	TS	EB	Date	N	TS	EB
Feb. 17	1	165	727	Feb. 11	1	168	597	Feb. 21	1	243	590
Feb. 18	1	171	733	Feb. 12	1	176	606	Feb. 24	1	239	581
Feb. 20	1	170	726	Feb. 13	1	184	617	Feb. 25	1	245	588
Feb. 26	2	163	723	Feb. 14	1	186	616				
Feb. 27	2	165	725	Feb. 17	1	184	612				
Mar. 2	1	166	724	Feb. 18	1	167	588				
				Feb. 19	1	169	603				
				Feb. 20	2	182	606				
				Feb. 21	1	179	599				
				Feb. 24	1	175	608				
				Feb. 25	1	192	619				
				Feb. 27	1	172	602				
				Feb. 28	2	169	601				
				Mar. 3	2	177	609				
				Mar. 4	1	166	584				

N = number of low values excluded.

daily means for tensile strength is due to day-to-day variation in some factor or factors not yet accounted for.

(ii) ELONGATION AT BREAK

The results for elongation at break have been treated in the same way as those for tensile strength (Table 15). The normal results are those for all the specimens giving normal tensile strength figures, it being found that abnormally low tensile strength and breaking elongation always occurred together. It may

TABLE 15

ELONGATION AT BREAK (PERCENTAGE)

		A, rings	B, rings	A, dumb-bells	B, dumb-bells
Complete results	Series mean	723.3	596.0	704.2	58.43
	S.D. of individual results	15	26	20	14
	Calculated S.E. of daily means	5.5	9.5	8.2	5.8
	Observed S.E. of daily means	11	13	7.4	7.3
Normal results	Series mean	727.3	605.2	—	586.3
	S.D. of individual results	11	17	—	11
	Calculated S.E. of daily means	4.1	6.5	—	4.5
	Observed S.E. of daily means	8.2	10	—	5.9

be added that by taking the normal results for all four series of tests together, the deviations of the daily means from their respective series means were found to give a frequency distribution curve closely resembling the normal probability curve.

The standard deviations for the complete results may be compared with figures given in, or deducible from, published data, *viz*: 18, 13, 18, and 17 per cent for rings[7] and 17 per cent for dumb-bells[9].

The observed standard error of the daily means is greater, except with A dumb-bells, than the value calculated from the standard deviation of the individual results.

The values of F are:

	A rings	B rings	A dumb-bells	B dumb-bells
Experimental: complete	4.05	2.31	1.21	1.58
Experimental: normal	4.00	2.89	—	1.71
Value for 5% probability	1.67	1.72	2.15	1.80
Value for 1% probability	2.04	2.15	3.00	2.28

In the case of ring specimens, therefore, the differences between observed and calculated standard errors are highly significant, since the odds against their being due to chance are more than 100 to 1. With dumb-bell specimens the differences are not significant. These conclusions apply to both complete and normal results, although the actual magnitude of the standard deviations and errors is always smaller for the normal results, as would be expected.

The results, therefore, resemble those for tensile strength in that the variation among results obtained on the same day appears to be responsible for a considerable part, though not all, of the variation between the means of different days' tests. Possible causes of the excess day-to-day variation are discussed in paragraph (vi) below.

It has not been thought worth while calculating exactly the standard error of the 2/4 means, as was done with tensile strength, but from the figures in Table 15 it is estimated, by analogy with the tensile strength results, that this is about 8–10 per cent, except for B rings (about 13 per cent). The higher value for the latter is in agreement with the observation that these rings were less cleanly cut than the other test-pieces.

(iii) ELONGATIONS AT CONSTANT LOADS, AND MODULI

An examination has been made of the data for elongations at 50 and 100 kg. per sq. cm. and for moduli at 300 and 500 per cent elongations only, as these give an adequate idea of the accuracy of the test procedure. Tables 16 and 17

TABLE 16

ELONGATIONS AT CONSTANT LOADS, (PERCENTAGE)

	A, rings		B, rings	
	E50	E100	E50	E100
Series mean	544.8	645.7	356.8	484.8
S.D. of individual results	2.3	2.1	2.6	3.5
Ditto (% of mean)	0.42	0.33	0.73	0.72
Calculated S.E. of daily means	0.8	0.75	0.9	1.2
Observed S.E. of daily means	3.1	3.2	3.4	4.0
S.D. of measurement	1.3		1.4	

TABLE 17

MODULI

	A, dumb-bells		B, dumb-bells	
	M300	M500	M300	M500
Series mean (kg. per sq. cm.)	21.2	62.4	53.0	161.8
S.D. of individual results (kg. per sq. cm.)	0.6	1.7	1.5	4.5
Ditto (% of mean)	2.9	2.7	2.8	2.8
Calculated S.E. of daily means (kg. per sq. cm.)	0.25	0.65	0.6	1.9
Observed S.E. of daily means (kg. per sq. cm.)	0.6	1.4	1.3	4.7
Ditto (% of mean)	2.7	2.2	2.5	2.9
S.D. of measurement, % of mean	2.5		1.8	

give the results for series means, standard deviation of individual results, and the calculated and observed standard errors of the daily means.

The observed percentage standard deviations for modulus are markedly smaller than published figures of 6.9 and 6.1 per cent for moduli at 300 and 500 per cent respectively[9].

It will be noted that, whereas the deviations and errors for elongations at constant loads are roughly the same for both rubbers and at both loads, those for modulus are approximately constant percentages of the respective mean values.

In every case the observed standard error of the daily means is very significantly greater than that calculated from the standard deviation of individual results. The values of F are:

	Rings		Dumb-bells	
	E50	E100	M300	M500
Rubber A: Experimental	15.2	20.7	5.8	4.6
1% probability	2.04	2.05	2.28	2.28
Rubber B: Experimental	19.5	18.3	4.8	6.1
1% probability	2.15	2.15	2.28	2.28

In every case, therefore, the difference between observed and calculated standard errors is so great that the odds against its being due to chance are much more than 100 to 1. The difference is especially large with ring specimens, where the observed error is about 4 times the calculated figure. There is, therefore, definite evidence that measurements of elongation at constant load and of modulus are affected by some factor, other than those already allowed for, that varies from day to day. The possible nature of this factor is discussed in paragraph (vi) below:

With these properties it is possible to carry the analysis of the sources of error a step further, since an estimate can be made of the proportion of the standard deviation that arises from errors of measurement, as distinct from variations in the rubber. It is known from previous experience of the rubbers tested that small variations in period of vulcanization cause the stress-strain curve, at least between 50 and 100 kg. per sq. cm., to move so as to remain parallel to itself. It is found, also, that such variations produce approximately the same percentage changes in the moduli at 300 and 500 per cent elongations. Consequently, small variations in vulcanization would not alter the difference between the elongations at 50 and 100 kg. per sq. cm. or the ratio of the two moduli. Actually, it is found that these quantities do vary among specimens tested on the same day. As this variation must arise from errors of measurement, it has been used to estimate these errors, by the following methods.

(1) *Elongation at Constant Load.*—The standard deviation of the differences between the elongations at 50 and 100 kg. per sq. cm. has been calculated by the mean range method from the variation of this difference within each day's test. If it is assumed, which is doubtless approximately true, that the errors of measurement are about the same for the elongations at 50 and 100 kg. per sq. cm., the resultant standard deviation for each elongation (*standard deviation of measurement*) is $1/\sqrt{2}$ times the standard deviation of the difference.

(2) *Modulus.*—The standard deviation of the M500/M300 ratio has been calculated by the mean range method from the variation of the ratio within each day's tests, and then expressed as a percentage of the mean ratio. Assuming that the percentage error of measurement is the same for M300 as for M500,

the standard deviation of measurement (as percentage of the modulus) is $1/\sqrt{2}$ times the standard deviation of the ratio.

Values so obtained are given at the foot of Tables 16 and 17. Comparison with the standard deviation of individual results shows that in the case of ring specimens (Table 16) about half of the total variation in elongation at constant load is attributable to errors of measurement, the other half being therefore ascribable to variation among the specimens used in each day's tests.

With dumb-bells (Table 17) a larger proportion of the total variation is due to errors of measurement. The reason for this is seen by converting the values for standard deviation of measurement from percentage change in rigidity to the corresponding change in elongation at constant load, which is easily done by using the slopes of the stress-strain curves at 300 and 500 per cent elongation. The figures so obtained are 4.3 and 3.2 (percentage elongation) for rubbers A and B, respectively, which are much greater than the figures of 1.3 and 1.4 obtained for ring specimens of the same rubbers (Table 16). The larger errors for the dumb-bell specimens clearly are due to the difficulty of accurately measuring the elongation between gauge marks, originally 1 inch apart, by holding a scale alongside the specimen.

(iv) HARDNESS

Results calculated in the usual way are given in Table 18.

TABLE 18

HARDNESS NUMBER

	A, rings	B, rings	A, dumb-bells	B, dumb-bells
Series mean	138.5	93.8	113.1	79.9
S.D. individual results	3.1	2.3	1.0	1.0
Calculated S.E. of daily means	1.6	1.1	0.5	0.5
Observed S.E. of daily means	1.8	1.5	1.8	1.4

In every case the observed standard error of the daily means is greater than that calculated from the standard deviation of individual results. The values of F for the dumb-bell specimens (13.0 and 7.8 for A and B, respectively) are much greater than that corresponding to 1 per cent probability (2.45), showing that there is some cause of day-to-day variation not yet accounted for. With the ring specimens, the values of F (1.25 and 1.85) do not exceed the 5 per cent probability value (1.85), so a definite conclusion cannot be drawn in this case.

It might have been expected that, with rubber A, where a different specimen was used for each day's test, the observed standard error would be considerably greater than with B, where the same specimens were used throughout. When the errors are expressed as percentages of the corresponding mean results, however, no such difference is observed.

(v) PERMANENT SET

The results for permanent set show again that the observed standard error of the daily means is greater than can be accounted for by the variation among individual results obtained on any one day, and here the differences are highly significant, since F equals 7.1 and 4.4 for A and B respectively, the value for 1 per cent probability being 2.3. Evidently, therefore, some factor in the test technique is varying from day to day.

TABLE 19

PERMANENT SET (PERCENTAGE)

	A, rings	B, rings
Series mean	3.13	4.52
S.D. of individual results	0.11	0.23
Calculated S.E. of daily means	0.06	0.12
Observed S.E. of daily means	0.16	0.25

It is interesting to compare these results with those of the investigation on the accuracy of the cone method of measuring permanent set of rings[3]. It was there found that the standard deviation of repeat measurements of the diameter of the same ring by the same person at approximately the same time was about 0.07 per cent. This may be compared with the present values for standard deviation of individual permanent set measurements, the excess of these figures over 0.07 per cent giving some idea of the errors arising from the variations (among the four rings tested on one day) in the properties of the rubber, initial diameter of the rings, and the stretching and recovery treatments. The results of the previous investigation showed also that the standard error of means, each of four measurements, obtained on the same ring by the same person on successive days, is about 0.12 per cent, this figure being apparently not very dependent on the nature of the rubber. As all the permanent set tests in the present work were carried out by one person, the excess of the observed standard errors of the means over 0.12 per cent shows the approximate magnitude of the errors introduced by the variation, within each day's tests and from day to day, of the factors mentioned above.

(vi) SOURCES OF EXCESS DAY-TO-DAY VARIATION

It has not yet been possible to explain fully the excess of the day-to-day variation above that which would be expected from the variation within the results obtained on the same day, but attention may be drawn to two facts which point to possible causes.

In the first place different operators appear to differ greatly in the consistency of their results from one day to another. This is seen in the results for the A rings (Table 19). The operators shown under TS and EB are those who observed the loads and elongations, respectively, and the operators paired together in each column are those who worked together in the tests.

It will be seen that the pair A–P obtained unduly variable results for both tensile strength and breaking elongation. In the case of tensile strength, indeed, the variable results obtained by this pair of operators accounts entirely for the excess of observed over calculated standard error for the whole set of results, shown in Table 13. The tensile strength results obtained by the pairs A–J and J–A vary no more from day to day than would be expected from the variation within each day's results, and in their elongation results the excess day-to-day variation is barely significant.

The differences between the pairs A–P and J–A are highly significant, as the odds against their occurring by chance are 100 to 1 in the case of elongation at break and even higher in the case of tensile strength. These differences are not due to the operators differing in consistency within each day, since the within-days standard deviation of tensile strength is exactly the same for A as for J, and that of elongation is only slightly greater for P than for A.

TABLE 19

DAILY MEAN TENSILE TEST RESULTS (COMPLETE) FOR A RINGS

Operators	TS (A–J)	EB (A–J)	TS (A–P)	EB (A–P)	TS (J–A)	EB (J–A)
	162	710	162	716	172	734
	166	723	175	730	168	729
	165	722	182	748	162	715
			145	701	156	716
			151	709	163	724
			178	740	170	721
			168	728	167	731
					159	715
					169	731
					164	726
Mean	164	718	166	725	165	724
Standard deviation of individual means	2	7	14	17	5.1	7.2

No significant differences in variability are found between the daily means for elongation at constant load obtained by different operators.

With the B rings, elongation readings were about equally divided between operators J and P, whose results differed very little in variability. Tensile strength readings on these rings, also the readings on dumb-bells of A and B, were mostly taken by the same operator, so that no reliable comparison between operators is possible.

It is just possible, of course, that the differences illustrated in Table 19 are accidental, in spite of their high statistical significance. They do, however, call attention to the possibility of personal idiosyncrasies which, if they are as large as the present results seem to indicate, merit further study.

A second possible cause of excess variation between different days' results is indicated by the M500 figures for A dumb-bells (Table 3). All the five values obtained during the second week are low (60.1–61.0) compared with the rest (62.2–64.1), and the odds are over 1,000 to 1 against this being a chance occurrence. There is a similar, but less well defined, tendency in the M500 figures for B dumb-bells, where the second and fourth weeks give rather lower figures than the first and third. An effect such as this could arise from the temporary development of sticking or friction in the test machine at or around a certain point on the load scale.

(vii) AVERAGING OF TENSILE STRENGTH RESULTS

An important matter on which the results of the present work can be used to give some information is the method to be used for averaging tensile strength figures.

The problem turns chiefly on the treatment of the low figures that usually occur in small proportion among the test results, as shown by the present work and by previous investigators[12].

Such low results can, and doubtless often do, arise from faults in the preparation of the specimen or from some defect in the test technique. They may arise also from faults already present in the material tested, although it is often not possible to decide which of these two causes is responsible.

In testing manufactured articles, *e.g.*, for specification purposes, there seems to be no reason for rejecting low results caused by faults in the article, because

these are an inherent part of the article and it is important to know of their presence. For research purposes, however, it may be argued that the value which it is desired to know is the most probable value, *i.e.*, the peak or mode of the frequency-distribution curve for a large number of results. It is not generally feasible to obtain enough results to construct such a curve; hence, a method is required for obtaining, from a small number of results, a value which will approximate as nearly as possible to the most probable value.

As the bulk of the values for tensile strength, that is, all except the abnormal low values, usually lie on a substantially symmetrical distribution curve, a simple arithmetic mean of these normal values gives a close approximation to the most probable value, as is shown by the following figures (the dumb-bells of A are omitted because the nonuniformity of the material renders the results unreliable):

	Tensile strength (kg. per sq. cm.)		
	A, rings	B, rings	B, dumb-bells
Mean of normal values	168.4	176.4	236.3
Most probable (modal) value	167	178	236

The problem therefore reduces itself to that of deciding which are the abnormal low values that should be rejected before taking the average.

A method has been described by Davis and Horrobin[10], but two objections may be raised to this:

(1) It is assumed that the standard deviation of tensile strength results is the same for all rubbers. This seems very unlikely, indeed, the following figures for standard deviation suggest that it varies considerably.

	kg. per sq. cm.	Percentage of mean TS
Cloth-marked dumb-bells[13]	5.5	3.26
Buffed dumb-bells[14]	14.0	3.3
Present investigation	13 to 17	5.5 to 10
Dumb-bells of heavily loaded magnesium carbonate mix[15]	19.0	10.8
Rings[7]	26	16

Moreover, in most work it is not feasible to determine the standard deviation, with adequate accuracy, of every rubber tested.

(2) Even if the difficulty noted above could be overcome, the method might still be considered too time-consuming for use in a routine testing laboratory dealing with very large numbers of results.

For the type of work referred to in (2) a very simple and rapid method capable of giving reasonably accurate results is required. The simplest type of method is one in which one or more of the lowest figures are rejected and the rest averaged. From the small number of abnormal low results indicated by Figures 3, 4, and 6 it is obvious that the proportion which need be rejected is small. Thus, where four specimens are tested, the rejection of the lowest two, as has hitherto been standard practice in the R.A.B.R.M. laboratories, is excessive. This is evident also on comparing the means obtained by the various methods, bearing in mind that the true value lies in the region of values I and II; the 2/4 means obviously give too high a value.

	Tensile strength (kg. per sq. cm.)			
	A, rings	B, rings	A, dumb-bells	B, dumb-bells
I. Mean of normal values	168.4	176.4	(*a*)	236.3
II. Most probable value	167	178	265	236
III. Mean of 2/4 means	173.9	181.7	276.2	242.2
IV. Mean of all values	165.2	170.0	259.0	234.0

(*a*) Abnormal values cannot be separated.

On the other hand, to reject none would lead in quite a number of cases to the inclusion of abnormal low values and hence to too low a mean.

A simple alternative is, therefore, to reject the lowest one of the four, and average the rest. This eliminates abnormal low figures in all cases except where the four results include two or more abnormally low ones. Such cases are obviously very uncommon; thus, in the present work, there is not one case out of the 69 sets of results where half of the set are abnormally low. The main objection is, therefore, that the method rejects some satisfactory results. This, however, is not usually serious, because in a set of four results distributed according to the normal probability law with a standard deviation of 6 per cent (the average for the normal results in Table 13), the omission of the lowest value will raise the average by 2 per cent only. For most purposes, bearing in mind the other sources of error in tensile testing, there can be no serious objection to this. Moreover, this error, as also that arising from the very occasional occurrence of abnormally high results, could be avoided by rejecting both the lowest and the highest values, and averaging the rest, a procedure that would be applicable to any fairly small number of results, say not more than 8.

When great precision is required, or statistical treatment of the results is contemplated, objection might be raised to the omission of the lowest value out of four, because the resulting increase in the mean is a fairly large proportion (2/3) of the standard error of this mean, and because it is difficult to estimate the accuracy of a mean so obtained.

The practice adopted by the American Society for Testing Materials[16] is to average the highest figure and those figures (normally 1 or 2) that are not more than 5 per cent below it. This method seems to be based on the assumption that the highest obtainable figure is the correct one, which is obviously not true in the case of a property whose values are distributed more or less in accordance with the probability law. Although the method when applied to a small set of results, *e.g.*, 3 as in the normal A.S.T.M. procedure, usually gives a fair approximation to the true value, it should certainly not be applied to large sets of results, for the greater the number of results in the set the more does the calculated mean exceed the true value. Moreover, if the values first obtained happen to contain one unusually high value, many more specimens may have to be tested to obtain another value within 5 per cent of it and then the mean of these will not be near the true value.

IV. SUMMARY AND CONCLUSIONS

1. An investigation has been made into the accuracy with which measurements of tensile strength, breaking elongation, elongation at constant load, modulus, permanent set, and hardness can be repeated on successive days, using specimens taken from the same sample of rubber.

2. There is evidence that the gradual blunting, during normal use, of the knives used for cutting ring or dumb-bell specimens may appreciably reduce the tensile strength of the specimens.

3. After allowing for the apparent effects of blunting, aging of the rubber, and day-to-day variations in test temperature, the variability of the results has been examined by determining (1) the variability within each day's results (standard deviation of individual results); (2) the variability among the means of different days' results (observed standard error of daily means); and (3) the variability of daily means that would be expected to arise from (1) (calculated standard error of daily means).

4. In nearly every case the observed error of the daily means is greater than calculated value, showing that the results are affected by some factors (other than those already allowed for) that vary from day to day. It is not possible at present to say definitely what these factors are, although two causes of variation are suggested. In many cases, however, particularly with tensile strength and breaking elongation, a considerable part of the variation among daily means can be ascribed to the variation among individual results obtained on one day.

5. Examination of the frequency distribution of the tensile strength results shows that the majority (90–98 per cent) usually form a substantially symmetrical curve of the normal type, the remainder being abnormally low values, though not necessarily unreliable values. If the low values are excluded, the standard deviations and (in most cases) standard errors are reduced, but the conclusions deduced from them remain substantially unchanged.

6. According to the usual mathematical convention, an observed difference between two means of less than $t/\sqrt{2}$ times the standard error of either (assumed to be the same for both) is not significant, *i.e.*, cannot with reasonable certainty be called a real difference. The value of t is about 2 if the standard error is calculated from a large number of observations, but greater than 2 if the number of observations is small[6]. For the rubbers and test methods here dealt with, therefore, differences less than about the following amounts, between means obtained in the same laboratory, are not significant (the figures given are only approximate averages; more exact values for (*a*) and (*b*) could be deduced from the tabulated figures for observed and calculated standard errors respectively; t has been taken as 2).

	(*a*) Tested on different days		(*b*) Tested on same day	
	Actual value	% of mean	Actual value	% of mean
Tensile strength:	kg. per sq. cm.		kg. per sq. cm.	
Mean of 6–8 values	20	9	15	7
Ditto, excluding low values	17	7	12	5
Mean of 2 highest out of 4 values	22	10	17	8
Breaking elongation (mean of 6–8 values)	25%	4	20%	3
Elongation at constant load (mean of 6–8 values)	10%	—	3%	—
Modulus (mean of 6–8 values)	—	7	—	3
Hardness number (mean of 4 values)	4 units	4	2–3 units	0.5–1
Permanent set (mean of 4 values)	0.6%	15	0.2–0.3	6

7. In the case of elongation at constant load and modulus, the variability among individual tests is analyzed into that due to inequalities in the rubber and that due to errors of measurement. The latter is much greater for dumbbells, where elongation is measured by a scale held against the specimen, than for rings, where readings are taken from a percentage elongation scale.

8. The averaging of tensile strength results is discussed with special reference to the treatment of low figures, a distinction being drawn in this connection

between the requirements of tests for commercial and for research purposes. The view that the highest obtainable value is the correct one is held to be fallacious, the modal or most probable value being considered as the true one. It is unnecessary to reject as many as two of the lowest values out of a set of four. Rejection of the lowest one, or even the lowest and highest ones, is preferred as a simple and rapid routing method, although the more elaborate method of Davies and Horrobin[10] has advantages in cases where time and other circumstances permit and the necessary data are available.

ACKNOWLEDGMENT

Acknowledgment is made of the assistance given by R. G. Newton in the statistical examination of the results and in drawing attention to the possible causes of day-to-day variation discussed in paragraph III (vi).

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STATISTICAL CONTROL IN THE PHYSICAL TESTING OF RUBBER *

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It is a commonly accepted fact that complete reproducibility cannot be obtained in the manufacture of commercial products. It is equally true, but not so commonly accepted, that repeated tests on samples drawn from a completely homogeneous master sample will not yield completely similar results.

This fact is not evident in many of the usual measurements. For example, suppose that one were to measure repeatedly the diameter of a cylindrical shaft with a micrometer. The results obtained, if the measurement were made to the nearest 0.001 inch, would appear identical, and thus it would seem that completely reproducible results were obtained.

The other extreme is, perhaps, the measure of tensile strength of rubber. Assume for the moment that we have a completely homogeneous batch of some standard rubber compound which has been cured in such a way that the temperature and the pressure exerted are everywhere exactly the same. Next, assume that we cut out a large number of dumbbell pieces from this sheet of cured rubber with a single die and test each piece for tensile strength. Anyone with experience in rubber processing would, I am sure, agree that the tensile results from such test-pieces would not be identical.

The difference between the measurement of a cylindrical shaft and a rubber sample is, however, only one of degree, for if we had attempted to measure with an ordinary micrometer the diameter of the shaft to the nearest 0.00001 inch instead of to the nearest 0.001 inch, completely identical results would not have been obtained. In fact, W. A. Shewhart, who is considered the founder of the industrial application of statistics, points out that a shaft does not have a diameter, but has, for any given length, an infinite number of diameters. Thus, regardless of type of measurement, variation exists in results obtained.

In many products variation in observed results due to testing methods is of negligible importance. In the physical testing of rubber, variations in test results is extremely important. The proper evaluation of rubber compounds through physical testing requires that variation in test results due to testing be adequately determined and properly controlled.

APPLICATION OF STATISTICAL ANALYSIS TO INDUSTRY

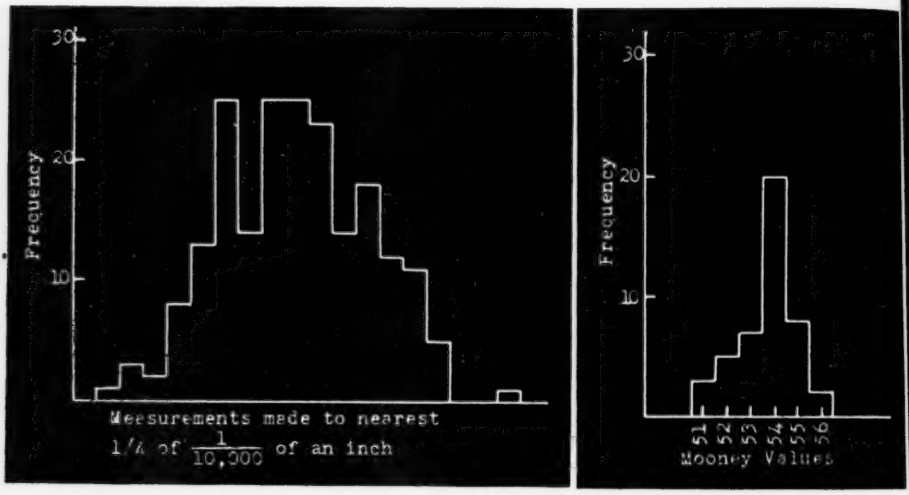
A relatively recent application of the science of statistics to industry is found in the determination and the control of observed variability in test results. It is my purpose to discuss in general terms the methods by which this is done.

Two types of test-samples need to be considered. In one instance a sample can be measured repeatedly without destruction or distortion of the measured sample. The measurement of the diameter of a shaft is an example. In other instances measurement either destroys or distorts the sample in such a way that only a single measurement can be made. An example of the latter is the tensile or modulus measurement on a dumbbell cut from a rubber sample. In the first instance we can consider the variation observed in the repetitive measurements of the sample; in the second instance we may possibly, through

* Reprinted from the *India Rubber World*, Vol. 114, No. 5, pages 653–655, 665, August 1946. This paper was presented before the Rubber Division of the Canadian Institute of Chemists at Toronto, Ontario, June 25, 1946.

a certain degree of idealization, discuss the variation encountered in successive measurement of samples drawn from a completely homogeneous master sample.

In either instance a certain pattern of variation will be observed. In Figure 1 are exhibited two of these patterns of variation: (1) the pattern of variation of 200 successive measurements of the diameter of a small round carbon rod, (2) 45 measurements of plasticity taken on 45 successively tested samples drawn from a master sample of GR-S. The patterns of variation exhibited in Figure 1 are the basis for the statistical work used in controlling physical testing of rubber. In most if not all instances, this pattern can be adequately described by a normal distribution. This is true whether there is repetitive testing on a single sample or testing on successive samples drawn from a master sample. Typical normal distributions are shown in Figure 2



A. Histogram of 200 measurements on a carbon rod.

B. Histogram of 45 Mooney values on X-55 bale.

FIG. 1.—Pattern of variation for 200 measurements on carbon rod and on 45 Mooney values on a bale of GR-S.

superimposed on the observed patterns of variation already displayed in Figure 1.

Any normal distribution is completely determined by two parameters[1]. These are the mean, a common symbol for which is $\bar{x}$, and the standard deviation, the common symbol for which is the Greek letter σ. The mean, X, is the measure of central tendency of distribution and can be said to "position" the distribution. The standard deviation, σ, is the measure of spread of the distribution. For any normal distribution complete information is derived from the two parameters, X and σ. An extremely important item of information is the percentage of frequencies expected between $X \pm \sigma$. Because this is known for a normal distribution and because the normal distribution so frequently describes the patterns of variation observed in repetitive testing, the standard deviation of such a pattern has been accepted as a measure of this variation. The term *testing error* has become very popular in describing this variation. Testing error, as we use it, is defined as the standard deviation of the distribution of either repeated tests made on a single sample or successive tests made on successive samples drawn from a completely homogeneous master sample.

EXAMPLES OF USE OF TESTING ERROR

Before discussing some of the difficulties encountered in arriving at an adequate estimate of the testing error for any particular test of physical rubber it will be advantageous to discuss some of the uses of this measure of testing variability. In the simplest case (statistically speaking) involved in the physical testing of rubber, that is, in the running of a Mooney test, we find an example. Suppose the control laboratory is asked to test samples A and B for some factory or for some experimenter. The Mooney result on sample A is 50 and the result on B is 53. Is sample A softer than sample B? This ques-

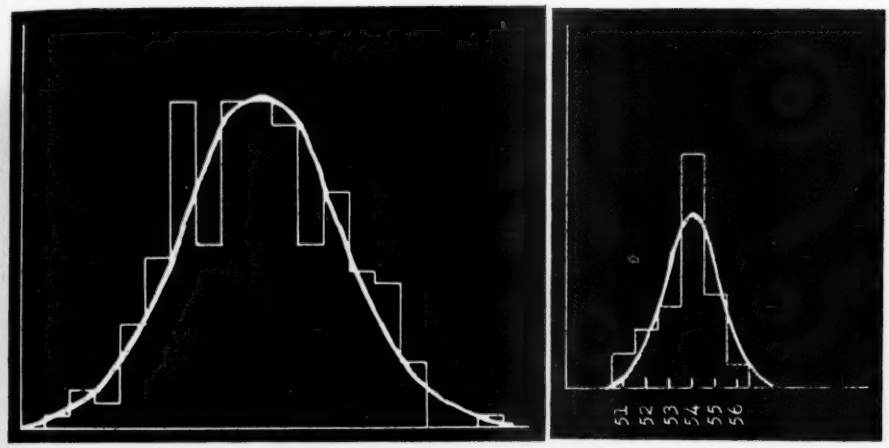


FIG. 2.—Normal distribution curve superimposed on patterns of variation of Figure 1.

tion cannot be properly answered unless the reliability of the Mooney test, as carried out in the laboratory producing these results, is known. Suppose the testing error in this particular laboratory is known to be 1.6. Then there is no assurance that a difference exists between sample A and sample B. However, if the testing error of the laboratory under consideration is known to be 0.8 Mooney, a difference as large as 3 Mooneys would be observed so infrequently that complete assurance is had that sample A is really softer than sample B. This point illustrates one of the uses of testing error in the interpretation of test results.

Another use is in the determination of how far the observed sample result may be from the true value of the sample. For instance, a 300 per cent modulus result of 1250 lbs. per sq. in. is observed. This is not taken as the true or ideal value of the material from which the sample is drawn because it is well known that variations due to compounding, curing, and tensiling have an effect on the test results. But the man who submitted the sample is extremely interested in determining within what distance of the observed value the true value falls. A very good estimation of this range can be made if the test is running under control with a known testing error. If the testing error on 300 per cent modulus is 40 lbs. per sq. in. chances are 19 out of 20 that the true value is within 80 lbs. per sq. in. of the observed value.

DETERMINATION OF TESTING ERROR

In the Mooney plasticity test the estimation of a pattern of variation, and consequently the testing error, is relatively simple. The test is made in a

single step. A large mass of thoroughly mixed homogeneous material can be the source of numerous samples. These samples can be run consecutively. A frequency distribution of these samples is an estimate of the pattern variation expected from this test. Such a frequency distribution was shown in Figures 1 and 2.

However, this method of estimating the pattern of variation even for a simple (from a statistical viewpoint) test like the Mooney test has certain deficiencies. It does not take into consideration variations from day to day caused by any number of factors affecting the test which, although relatively constant during a short period, have a significant effect on Mooney results over a longer period. Therefore a better estimate of a pattern of variation would take into account the time element. Rather than run a large number of successive tests at one time, the homogeneous samples could be run two or three a day for several days. In Figure 3 we have displayed the results of samples thus run. Points No. 13 and No. 14 reflect an obvious shift in level of Mooney values.

Means are at hand, however, to eliminate the effects of these shifts in level from our estimate of the pattern of variation. In Figure 4 is displayed a pattern of variation for the Mooney machine which has been found to be accurate. Accepting for a moment the distribution displayed in Figure 4 as being a fair estimate of the pattern of variation for this test, we propose to show how such a test is controlled by statistical means. The two horizontal lines drawn at the values 48.4 and 51.6 encompass practically all, *i.e.*, 95 per cent, of the results obtained from the successive tests on the standard sample. These two values are then set up as limits on the variability of this standard sample. A control chart is constructed with these limits. This has already been displayed in Figure 3.

Once the chart is set up, the standard material is tested periodically. This test may be once per shift, twice per shift, or at some other interval. Each time a test is made on the standard, the value is posted on the chart. As long as the points fall between the lower limit of 48.4 and the upper limit of 51.6 in an acceptable pattern, the operation of the Mooney machine for material similar to the standard is deemed acceptable. The limits on the chart, set at two testing errors from the average quality level, are measures of the limit of variation expected. It can be seen that the first 12 points on the chart were all between the limit lines in an acceptable pattern. Point 13, however, has a value of 53. As a check, another sample was immediately run and found to have a value of 54 (see point 14). These two values both above the upper limit are construed as evidence that the operation of this machine was not as it had been during the preceding period.

Before any other tests were run, the equipment and methods of operation were examined. In this instance it was found that a new operator had been assigned to this job without adequate instruction. Because he had failed to allow the sample either sufficient conditioning time, or running time, the test results were high. When this condition was corrected, the standard again fell between the limit lines in an acceptable pattern until point 26 was observed below the lower limit. A recheck here revealed the next point to be within the limits. It was here assumed that point 26 was one of the 5 per cent expected to fall outside the limits through chance.

METHODS FOR PREPARING CONTROL CHARTS

Although it is not the purpose of this paper to delineate the routine methods of constructing control charts, the problem of obtaining the testing error of tensile

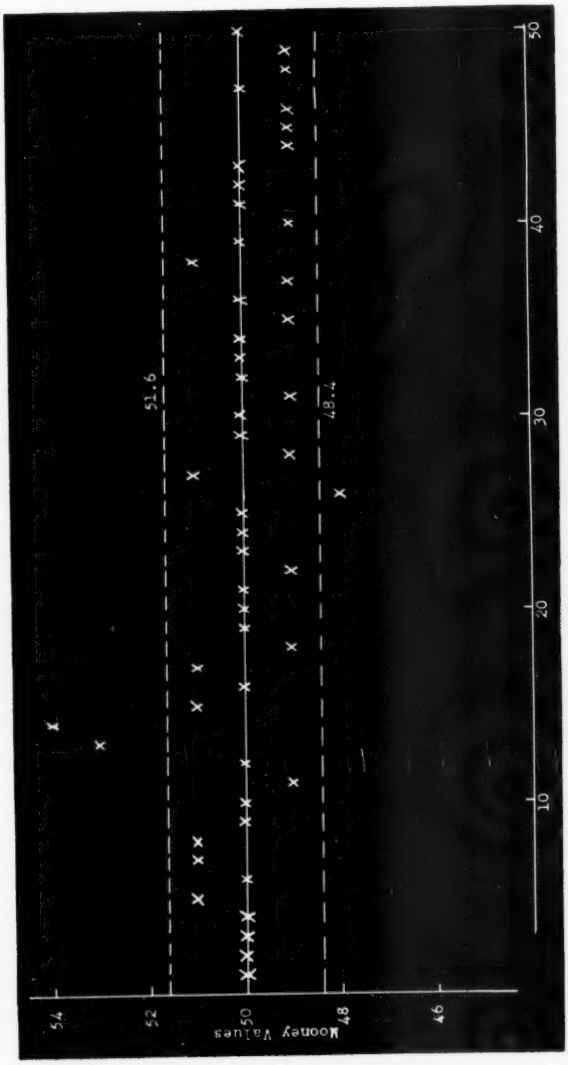


FIG. 3.—Control chart of Mooney values on GR-S standard.

results is of sufficient interest to warrant some exposition of the methods. A typical procedure in testing rubber for modulus, tensile strength, and elongation is to compound and cure a flat six-inch by six-inch by 100-gauge sample, cut and test three dumbbell pieces from the sample. The observed results involve variations due to compounding (in many instances), variations due to curing, and variations in tensiling. The term tensiling is used here to refer only to the operation of the Scott or other tensile machine. In some instances interest lies only in the cumulative variation caused by the three phases of the test. In other instances we are greatly interested in the variations due to each of the three phases.

Let us for the moment examine that variation due to tensiling alone. For all practical purposes the 100-gauge sample is homogeneous within itself with regard to compounding and curing. Therefore any variation between

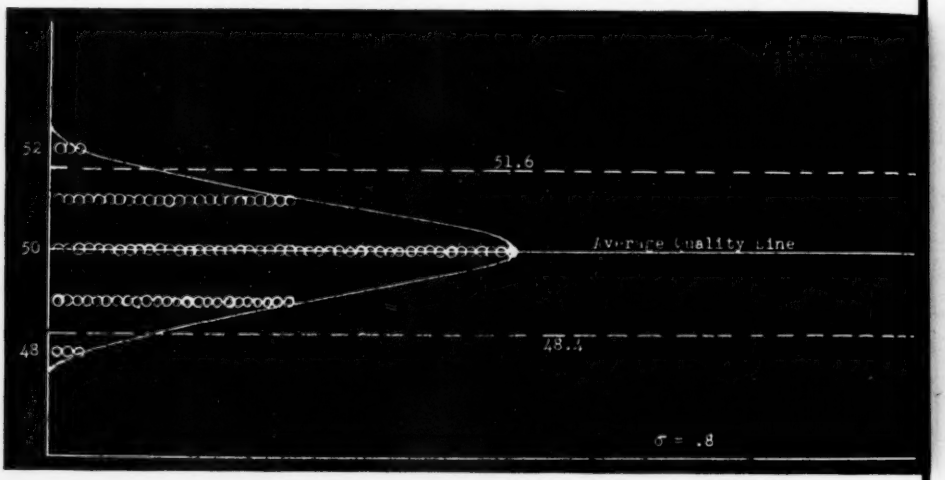


FIG. 4.—Estimated pattern on variation of Mooney values.

the three results on a single sample is due largely to variations of the tensiling operation itself.

This variation can be measured by the range of the sample, which is defined as the difference between the maximum and the minimum values in the sample. A definite relation exists between the average range of samples of a given size and the testing error. If the sample size is three, as is usually the case, the testing error, *i.e.*, the standard deviation or the pattern of variation or frequency distribution, is found by multiplying the average range by 0.59. This is the testing error of individual tensile readings. To determine the testing error of the averages of three readings, the average range must be multiplied by 0.341.

A very common mistake in the use of control chart procedures is the use of this particular average range for the tensiling operation as the basis for determining the testing error for the combined operations of compounding, curing, and tensiling. It should be emphasized that the variation thus found was only due to variations in the tensiling operation itself.

The lower half of Figure 5 is a chart of the ranges thus found. If it is desired to determine the variation due to curing and tensiling combined, the following procedure must be followed.

A master sample of some compound in which interest lies must be thoroughly mixed. Successive samples are drawn therefrom, and each sample is cured individually. Each sample is then died out into dumbbell pieces, probably three from each sample. The dumbbell pieces are then tested. The average result of the three pieces is then taken as the measure of the sample. Precautions must be taken against deterioration of the compounded standard. The selection of this standard will be based largely on its stability.

A little reflection makes it clear that this average result is the best estimate of an individual sample and is, therefore, to be considered as an individual reading. The variation between these averages is then the basis for estimating the pattern of variation, and the testing error where curing and tensiling are to be considered together as the test.

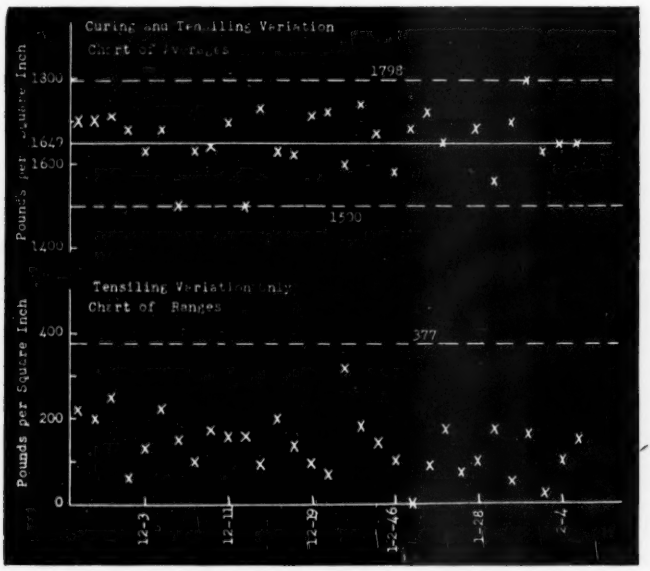


FIG. 5.—300% Modulus control chart (curing and testing).

The upper half of Figure 5 shows the values obtained for 300 per cent modulus by this procedure. Limit lines are shown, both in the upper and in the lower half of Figure 5. The nature of these limit lines is of considerable interest. Notice that the so-called chart of averages in the upper half has both lower and upper limit lines. So long as the points obtained on periodical tests of the rubber standard fall within these limits in an acceptable pattern, the equipment used for experimental or process tests of analogous compounds is considered to be functioning adequately. Furthermore the distance of the limit lines from the average line is set in such a way that one-half this distance is the testing error of the test. There is, therefore, at hand a measure of the reliability of results on process or experimental tests of a nature similar to the standard and made during the current period.

The limit lines on control charts are most frequently set by multiplication of an average range by some suitably selected factor. The average range is not, in this instance, the average range of the chart in the lower half of Figure 5, although the mistake of using this average range is almost uniformly made.

As previously mentioned, the range plotted in the lower half of Figure 5 is a measure of the variability within three dumbbells taken from the same sample. It does not, therefore, reflect in any way variations between samples.

This range for tests on the same sample has a different and distinct use. A frequently disturbing feature of tensile results is the observance of a large range. Every laboratory probably has a rule subjectively or arbitrarily arrived at for determining whether or not test results should be discarded. The chart displayed furnishes an objective means for doing this. Ranges of test results, as well as the individual test results, fall into a determinable pattern. The upper limit line can be established from this pattern. The upper limit on ranges is shown by the line on the chart of ranges displayed in Figure 5. As long as ranges fall below this line in an acceptable pattern, all the test results should be accepted. However, the observance of a range outside or above this line is taken as evidence that something is wrong with the test or the sample and hence indicates that the observed results should be discarded. Figure 5 is thus also a control measure for determining the acceptability of test results.

CONTROL CHARTS DETERMINE RELIABILITY OF RESULTS AND EQUIPMENT ACCURACY

We have now given a slightly oversimplified explanation of two control charts for use in a physical testing laboratory. A control chart can be set up for one or more reference standards on each of the physical tests made on rubber. These control charts act as guides in determining whether or not the equipment is functioning properly. The information derived from the data plotted on the control charts becomes the basis for evaluating the reliability of the test results put out by the physical testing laboratory.

These charts of reference standards can also be used profitably in determining the accuracy of the test equipment. Refer again to Figure 3. The average quality line is found at 50 Mooney. It is relatively easy to determine whether this is comparable to other plastometers in the same or other plants. If the true value of the standard used is found to be 45 instead of 50, not only are the standard samples, but all samples being incorrectly evaluated.

The same general principle can be applied to tensile testing. An adequate estimate of the true value is more difficult to obtain here than in some other tests, but can be satisfactorily obtained.

A common reaction to these methods is the feeling that physical testing equipment can be adequately checked and controlled by mechanical means such as calibration with weights and wires. Our experience has been that these methods are not adequate and are no substitutes for statistical control.

SUMMARY AND CONCLUSIONS

In conclusion, may I repeat that the statistical methods find a useful and important application in the control of physical testing of rubber. An attempt has been made to show how the physical testing of rubber might yield more useful information if these methods were adopted.

The illustrations and examples given have been of a very general nature. It is hoped, however, that they are of sufficiently fundamental nature to point the way to specific uses in any laboratory.

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A VISCOMETER FOR MEASUREMENTS DURING THIXOTROPIC RECOVERY. RESULTS WITH A COMPOUNDED LATEX *

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INTRODUCTION

Various studies have been made of the break-down of thixotropic structure by stirring, and of the time required for recovery of structure under conditions of quiescence. However, there are certain operations, such as painting or dipping, in which the quality of the finished product depends in part on the flow properties of a thixotropic liquid under small but finite forces operating immediately after a rapid deformation while thixotropic recovery is still in progress. The forces referred to are those of gravity and surface tension. The apparatus described in the present article is designed especially for studying the rheology of a thixotropic liquid immediately after a rapid deformation, and for determining, in particular, the rate of thixotropic recovery while the liquid is subjected to a low shearing stress. Experimental data are reported on a commercial type of compounded rubber latex.

To obtain essentially uniform shearing stress and rate of shear throughout the test material, a viscometer of the rotating cylinder type with small clearances between the cylinders is desired. It would be comparatively simple to design such an apparatus with driving speeds or driving torques which could be abruptly changed. However, it would not be easy to devise a set of bearings for the rotating cylinder which would function satisfactorily at high torques and yet would have sufficiently small friction to have a negligible effect on the observations when the torque is very greatly reduced. To avoid this difficulty, a viscometer has been designed in which the arrangement for stirring the liquid to break down its structure is distinct from the arrangement for measuring the viscosity.

APPARATUS

The apparatus consists essentially of a hollow cylinder, called the rotor, suspended by a steel torsion ribbon in a narrow cylindrical channel, called the stator, which contains the test material. The novel feature of this apparatus lies in the fact that the inner wall of the stator is rotatable with respect to the outer wall. Therefore, by rapidly oscillating the inner wall, the liquid in the viscometer can be stirred, that is, sheared at a high rate. The torsional rigidity of the suspension is sufficiently low so that the rotor practically moves with the liquid. In other words, it has roughly half the angular velocity of the inner wall of the stator. After stirring is completed, the inner wall remains stationary, and viscosity measurements are made with only the rotor moving.

* Reprinted from the *Journal of Colloid Science*, Vol. 1, No. 2, pages 195–208, March 1946. This paper was presented before the Society of Rheology, October 27, 1945.

Figure 1 is a photograph of the viscometer proper disassembled. It will be observed that the inner part of the stator (3) has a conical bearing at its lower end which fits into a corresponding conical bearing in the outer part (1).

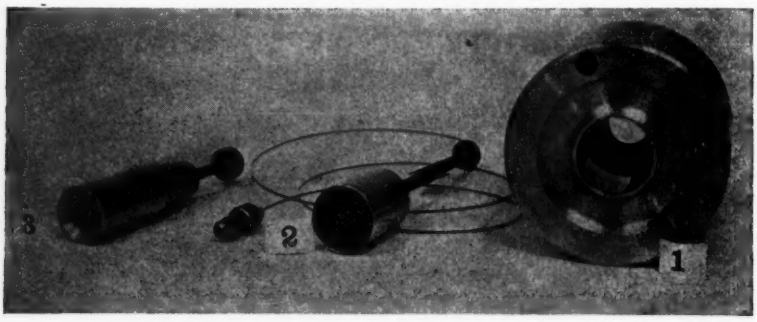

FIG. 1.—(1) Outer stator, (2) rotor, (3) inner stator.

A light film of oil serves to lubricate the bearing and, at the same time, makes the system watertight. A photograph of the complete assembly is shown in Figure 2.

The optical system includes 4 mirrors, mounted 90° apart on the rotor, and 4 light sources. With this arrangement, a record can be obtained of any num-

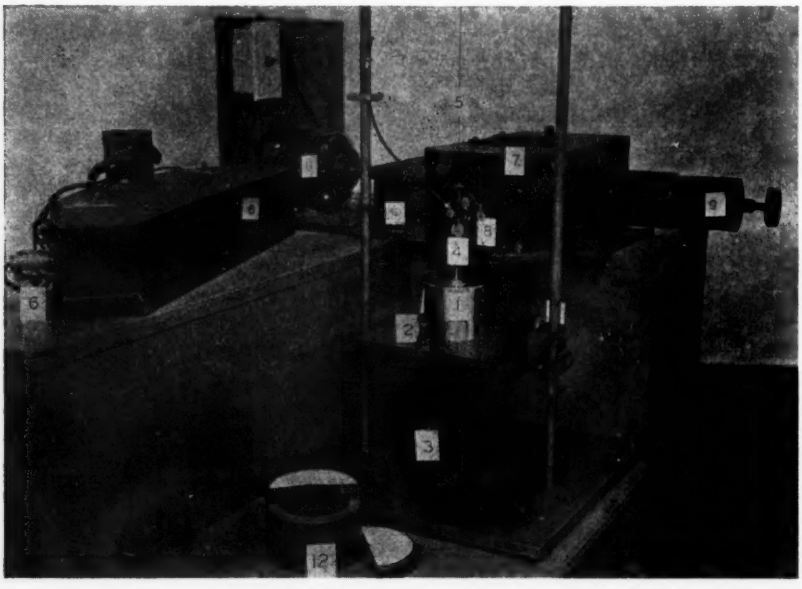

FIG. 2.—(1) Viscometer, outer stator. (2) Leveling screws. (3) Stirring handle, attached to rotatable inner stator. (4) Mirror on rotor shaft. (5) Suspension ribbon for rotor. (6) Lights, clear bulb, straight filament. (7) Camera box. (8) Lens and shutter. (9) Light-tight holder for drum in transporting to and from dark room. (10) Gear box. (11) Synchronous motor for rotating the drum. (12) Thermal insulation for viscometer. When in use, the rotating drum, carrying photographic paper, is mounted inside the camera (7) coaxial with the holder (9).

ber of revolutions of the rotor; for as one light spot is passing beyond the end of the photographic paper within the camera, the light spot from another of the 4 sources comes onto the paper at the other end.

THEORY OF THE VISCOMETER

With small, nearly equal clearances on both sides of the stator, the rate of shear and shearing stress are both nearly uniform throughout the liquid. Therefore, the viscosity also is essentially uniform and we may neglect variations in the viscosity. Let η be the viscosity, ω the angular velocity of the rotor in radians per second; R_1, R_2, R_3, R_4 the radii of the inner stator, the inside of the rotor, the outside of the rotor, and the outer stator, respectively; τ_1, τ_2, τ_3, τ_4 the tractions[1] at the corresponding points; L the immersed length of the rotor, and T the torque of the suspension. Then, by equations previously published[2]:

$$\eta\omega = \frac{\tau_1 + \tau_2}{2} \cdot \frac{R_2^2 - R_1^2}{R_2^2 + R_1^2} \tag{1}$$

Also:

$$\tau_1 R_1^2 = \tau_2 R_2^2 \tag{2}$$

Whence:

$$\eta\omega = \frac{\tau_2}{2} \frac{R_2^2 - R_1^2}{R_1^2} \tag{3}$$

Likewise:

$$\eta\omega = \frac{\tau_3}{2} \frac{R_4^2 - R_3^2}{R_4^2} \tag{4}$$

Now by setting T equal to the sum of the moments due to τ_2 and τ_3, we obtain from (3) and (4):

$$\eta = \frac{T}{4\pi L\omega \left[\dfrac{R_4^2 R_3^2}{R_4^2 - R_3^2} + \dfrac{R_2^2 R_1^2}{R_2^2 - R_1^2} \right]} \tag{5}$$

In addition to this equation for the viscosity, we require an equation for the mean traction. The mean traction in the inner space is $\tau_{1,2} = (\tau_1 + \tau_2)/2$; and in the outer space $\tau_{3,4} = (\tau_3 + \tau_4)/2$. In calculating the overall mean traction it is slightly better to weight $\tau_{1,2}$ and $\tau_{3,4}$ by factors proportional to the volumes of the two corresponding clearance spaces, these factors being $R_2^2 - R_1^2$ and $R_4^2 - R_3^2$. With this procedure the overall mean traction, τ, can be expressed in terms of $\eta\omega$ by using Equations (3) and (4) and two similar equations for τ_1 and τ_4. Elimination of $\eta\omega$ by use of Equation (5) then gives:

$$\tau = \frac{T}{4\pi L} \cdot \frac{R_4^2 + R_3^2 + R_2^2 + R_1^2}{\dfrac{(R_4^2 - R_3^2) + (R_2^2 - R_1^2)}{\dfrac{R_4^2 R_3^2}{R_4^2 - R_3^2} + \dfrac{R_2^2 R_1^2}{R_2^2 - R_1^2}}} \tag{6}$$

The dimensions of the present apparatus are: $R_1 = 1.045$ cm., $R_2 = 1.13$ cm., $R_3 = 1.175$ cm., $R_4 = 1.265$ cm., $L = 3.50$ cm. The torque constant of the suspension is 50.0 dyne-cm. per radian; and the moment of inertia of the rotor is 15.5 g.-cm^2.

METHOD OF OPERATION

The apparatus, at room temperature, is filled with the latex to be tested and some water is placed in the overflow channel of the stator. With the thermal insulation and cover in place, the water maintains high humidity under the cover and prevents skin formation by evaporation from the sample. The inner stator is oscillated by hand 8 to 10 times through an angle of about 90° at a rate of about 1 cycle per second. On the last oscillation, the handle is brought back to a positive stop against the frame of the viscometer; at the same time the upper end of the suspension ribbon is given a sudden twist proportional to the desired shearing stress, or traction. From this time on, the rate of rotation of the rotor is determined by the torque due to the suspension ribbon acting against the viscosity of the liquid. In the present work, the photographic records terminate at 20 to 40 seconds.

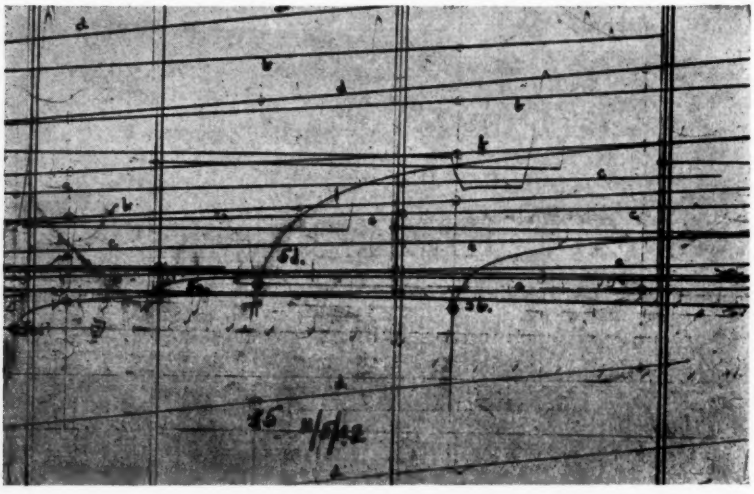

FIG. 3.—Photographic traces. Horizontal displacement is time, full scale = 10 seconds. Vertical displacement is rotation of the viscometer rotor.

Trace number	Traction, τ dynes per sq. cm.
5a	1.33
5b	4.00
5c	2.67
5d	5.33

Figure 3 shows four photographic traces on a single record paper. The velocity of the rotor at any instant is proportioned to the slope of the photographic trace. When the slope of the trace is changing rapidly, it is determined by fitting a tangent line to the curve. When the slope is nearly constant, best accuracy is obtained by measuring heights of the curve at different points.

EXPERIMENTAL RESULTS

Measurements were made on a commercial latex compound containing 47.5 per cent of total solids. The stirring process described above is obviously

not carried out with accurate controls. However, the reproducibility of the viscosity measurements show that with this latex the stirring process was sufficient to give reproducibility of breakdown of the thixotropic structure. The initial twist in the suspension ribbon was such as to develop an initial traction between 1.3 and 10.7 dynes per sq. cm. The traction in any experiment decreases with time as the rotor moves; but the percentage decrease was negligible in most cases and less than 6 per cent in the worst case.

Figures 4 and 5 show the viscosity as a function of time after the rapid shearing ceases for the range of tractions employed in viscosity measurement.

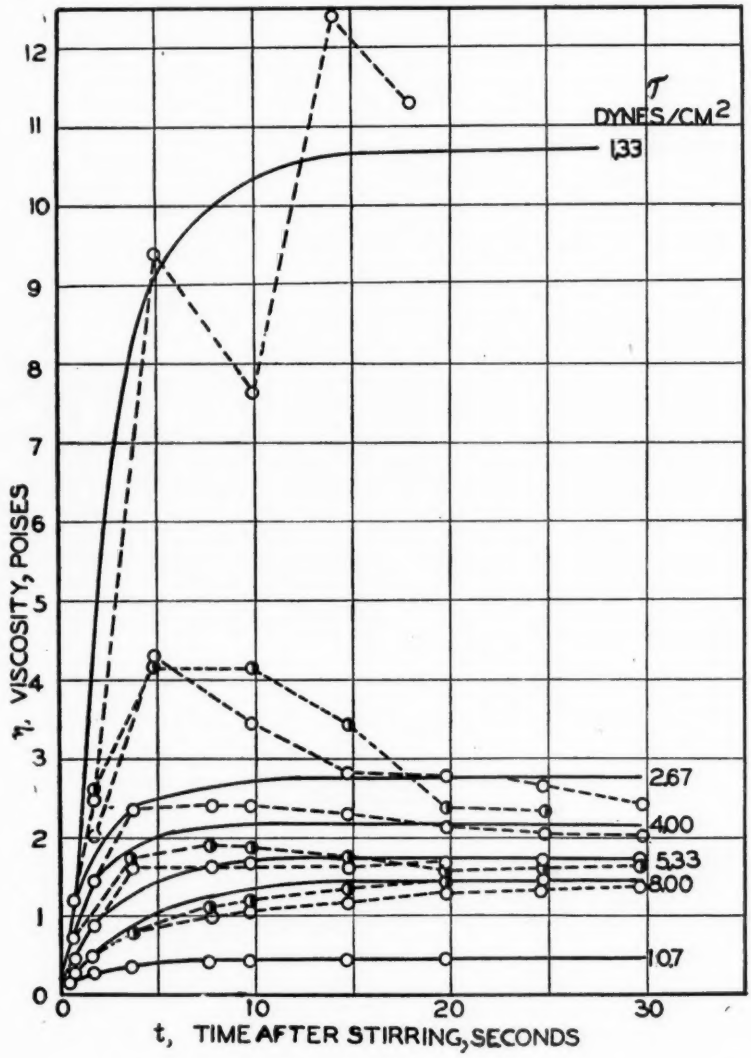

FIG. 4.—Observed and calculated viscosity *vs.* time after stirring, for various values of τ, the traction.

Within experimental error, all curves start, by extrapolation, at the same initial viscosity of approximately 0.05 poise. Thus, in the stirred state the latex is a Newtonian liquid. This is strong evidence that the thixotropic structure is completely broken down in the stirring procedure employed.

The viscosity begins to increase immediately after stirring. The initial rate of increase and the ultimate viscosity attained both decrease as the stress used in the measurement is increased. The maxima in the curves obtained with tractions of 2.7 to 5.3 dynes per sq. cm. are apparently reproducible and presumably real.

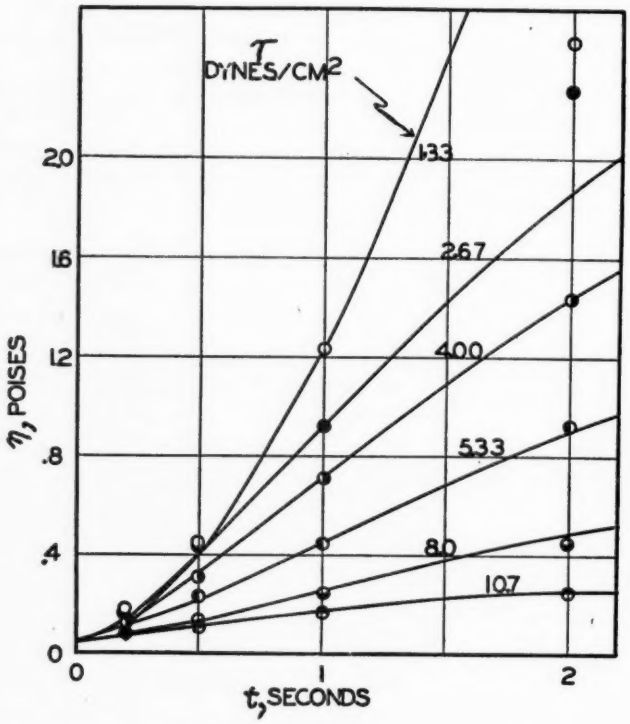

FIG. 5.—Observed and calculated viscosity *vs.* time after stirring, for various values of τ, the traction.

Figure 6 is a graph of the fluidity at 20 seconds after stirring *vs.* the traction. This curve suggests a yield stress at about 1.0 dyne per sq. cm. However, qualitative tests to detect a yield stress were not successful. In these tests, the apparatus was allowed to stand until the rotor assumed a steady position, when the rotor was turned through a few degrees and permitted to come back to a steady position again. There was no observable difference between the two final positions of the rotor. Since this procedure would reveal a true yield stress of 0.01 dyne per sq. cm., if it existed, we are forced to conclude that the yield stress suggested by Figure 6 is only apparent.

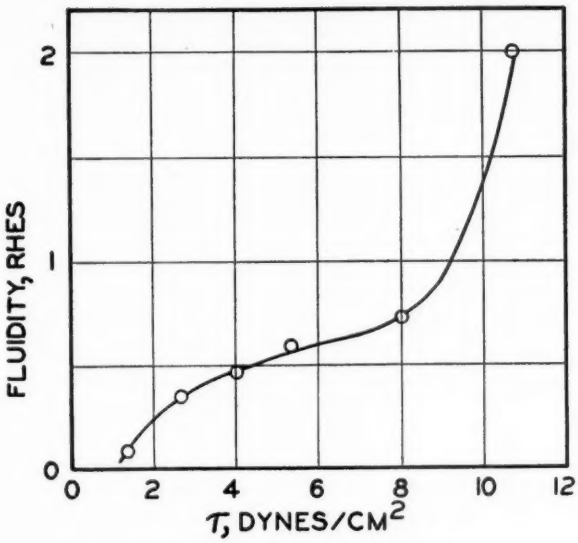

FIG. 6.—Fluidity at 20 seconds after stirring *vs.* traction, τ.

INTERPRETATION OF THE DATA

A commercial latex consists of a suspension of rubber latex particles and various compounding ingredients of various particle sizes and densities, stabilized by a suitable adjustment of the pH and the addition of various stabilizing agents. The large difference in viscosity between the active or stirred latex and the quiescent latex indicates that these suspended particles form weak agglomerates, which trap and immobilize considerable volumes of water, thus increasing the viscosity. In attempting a quantitative explanation of the experimental data, we shall assume that the agglomerization process after stirring follows the Smoluchowski theory of slow coagulation[3], and that the relationship between viscosity and fractional volume of the solid material, that is, agglomerated material including trapped water, follows an empirical viscosity equation based on Eilers' experimental data[4]. We must postulate also that the rate constant in Smoluchowski's coagulation equation varies with the traction in the liquid, since the higher the stress, the less the probability that two newly attached particles remain attached.

We assume that stirring breaks down all thixotropic structure, with the result that initially, that is, immediately after stirring ceases, the latex contains only elementary colloidal particles. Let there be N_0 such single particles per unit volume, of average volume, v, per particle. As agglomeration proceeds, we take account of the water trapped in the agglomerates by defining a swelling factor, f, by the equation:

$$v_n = nvf \tag{7}$$

where v_n is the volume of an agglomerate of n elementary particles. Then V, the effective partial volume of the solids including the immobilized water, is:

$$V = v[N_1 + f(N_0 - N_1)] \tag{8}$$

where N_1 is the number of single particles left unagglomerated at any time, t, after stirring ceases.

By Smoluchowski's kinetic theory of coagulation:

$$N_1 = \frac{N_0}{(1 + bt)^2} \tag{9}$$

where $b = kN_0$ and k is the velocity constant of the coagulation process. For "slow" coagulation, $k \sim 8\pi DrP$, where D is the diffusion constant of single particles, r is the particle radius, and P is the fractional number of impacts which result in permanent attachments. According to rough estimates, based on the value of b and other constants involved, $P \sim 10^{-1}$. This justifies describing the coagulation process as slow, even though the time to approach equilibrium is relatively short. Equations (8) and (9) give us

$$V = V_s \left[f - \frac{f - 1}{(1 + bt)^2} \right] \tag{10}$$

where $V_s = N_0 v$ = the true partial volume of the solids.

Lacking any direct measure of V, we must calculate it from the viscosity measurements. By combining Equation (10) with Einstein's viscosity equation, Smoluchowski obtained a relationship between time and the viscosity of a coagulating system, the increase in apparent volume of the coagulate being attributed to trapped water. However, there is no theoretical equation relating viscosity to V which has any validity at the large values of V involved in the present work. We must, therefore, employ an empirical equation. The best experimental data for our purpose are those obtained by Eilers in this measurement of the viscosity of aqueous suspensions of bitumen. An equation which fits his data very well has the form:

$$\eta_r = \sqrt{\frac{1 + .5V}{1 - V}} \exp. \left(\frac{1.25V}{1 - V} \right) \tag{11}$$

where η_r is the relative viscosity, or viscosity of the suspension/viscosity of water.

Figure 7 shows that this equation fits Eilers' experimental data quite well. Eilers' own equation fits slightly better; but it has a singularity, giving infinite viscosity, at $V = 0.78$. The corresponding singularity in Equation (11) is at $V = 1$. For this reason Equation (11) seems preferable, although the choice is largely a matter of judgment and involves the assumption that the dispersion in particle or agglomerate size is greater in the agglomerated latex examined here than in the emulsion prepared by Eilers. Fortunately the choice is not crucial; and any reasonable method of extrapolating Eilers' data would give essentially the same results in the present application.

There is a discrepancy at Eilers' last point, where $V = 0.7$; but the discrepancy is not large in terms of V. In this connection it may be remarked that there would be no point in concerning ourselves over small errors in V; for it is certain that at high partial volumes the viscosity will vary considerably with the size distribution of the particles, aside from questions of shape; and there is no reason for believing that the size distribution is the same in the agglomerated latex as in Eilers' bitumen suspensions. Equations (10) and (11) involve three variables, η_r, t and V; and three parameters, f, b and V_s. The parameters f and b may vary with the applied shearing stress, but V_s is the

same for all curves. If we take the intercept in Figure 5 as 0.052 poise, and the viscosity of water at room temperature as 0.009, we calculate the initial value of η_r to be 5.8. Then, by Figure 7, $V_s = .46$.

The values of f and b were determined for each experimental curve so that the theoretical curve would have the proper asymptotic limit and would pass through the experimental point at $t = 1$ second.

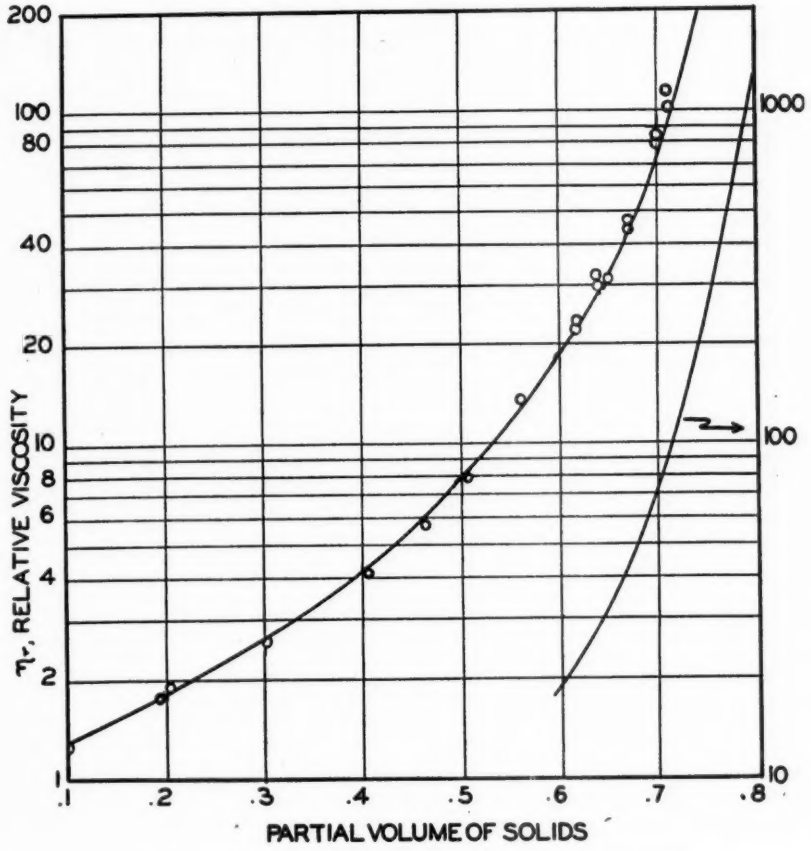

FIG. 7.—Eilers' experimental data on aqueous suspensions of bitumen spheres, and the empirical equation:

$$\eta_r = \sqrt{\frac{1 + .5V}{1 - V}} \exp. \left(\frac{1.25V}{1 - V}\right).$$

The various values thus determined are shown in Table I; the corresponding theoretical curves of η *vs.* t are the full curves shown in Figures 4 and 5. The curves agree satisfactorily with the data except for the maxima in some of the experimental curves. Especially noteworthy is the fact, revealed by Figure 5, that the theoretical curves for the smaller tractions show an initial slope less than the slope at 1 second, which is in agreement with the data. Since this feature of the data was not used in determining the parameters of the equations,

TABLE I

CONSTANTS OF THE AGGLOMERATION-VISCOSITY EQUATIONS

τ, dynes per sq. cm.	1.33	2.67	4.00	5.33	8.0	10.7
η_∞, poise	1000	260	220	175	150	50
η_1, poise	123	92	71	45	25	17
V_∞	.790	.750	.746	.740	.732	.676
V_1	.726	.706	.698	.668	.626	.592
f	1.796	1.705	1.696	1.683	1.664	1.537
b	1.546	1.652	1.524	1.042	.660	.676

$V_0 = 0.44$ = the partial volume at zero time after stirring. The viscosity of water at room temperature is taken as 0.009 poise.
τ = traction, or shearing stress, during viscosity measurement.
η_1 = viscosity at 1 second after stirring.
η_∞ = viscosity at infinite time.
V_0 = partial volume of agglomerates at 1 second after stirring.
V_∞ = partial volume of agglomerates at infinite time.
f = volume of flocculate/volume of solids in agglomerates.
$b = kN_0$.
k = velocity constant of agglomeration.
N_0 = initial number of single particles per cc.

the agreement in this case may be taken as additional evidence in support of the theory.

The maxima in the experimental curves reveal the presence of some important factor not included in the Smoluchowski theory of coagulation; and it appears highly probable that the large jump in η between $\tau = 1.33$ and $\tau = 2.67$ is due to this same factor. As a plausible explanation of the observed facts, the following hypothesis is submitted.

The initial agglomerates formed at a low traction are looser and contain more water than those formed at a high traction. These coagulates grow by accretion and coalescence until they occupy so much of the total volume that they are forced, in the shearing of the liquid, to approach very close or bump into each other. As a consequence of the resulting momentary localized high stress, the looser agglomerates break into fragments; and, in the final steady state, the only agglomerates left are those which are sufficiently dense and firm to withstand not only the average, continuous shearing stress, but also the occasional high stresses developed at bumping contacts. Thus, the maxima are to be attributed to the instability of the initial agglomerates under stresses which develop only after considerable agglomeration has occurred.

The apparent absence of a distinct maximum in the experimental curve at the lowest traction may indicate that even the bumping stresses in this case are insufficient to break up the loose agglomerates. This theory may appear to contradict the observation reported above that the quiescent latex has no yield stress greater than 0.01 dyne per sq. cm. However, the theory can be reconciled with this observation if we assume further that, at very low tractions, the agglomerates can undergo a very slow continuous deformation of a viscous type in which reattachments are formed within the agglomerate as fast as they are broken.

DISCUSSION

The partial volume of the solids in the latex is approximately 0.485, which is the figure obtained if we take the mean density of the solids to be 0.98. The value of 0.46 found for V_s therefore is slightly low, but is correct in magnitude and supports the assumption of no agglomeration in the stirred state.

Table I shows a general decrease in f as τ, the traction, increases. This trend reflects the variation in the initial slopes of the $\eta - \tau$ curves, and shows how the traction decreases the probability of permanence of new agglomerates.

The variation of f with τ is small in comparison with the variation of η, but the matter becomes comprehensible when we note that the slope of the $\eta - V_s$ curve in Figure 7 is very high.

The Smoluchowski theory[3] assumes that eventually all material in the suspension coagulates. Undoubtedly this assumption is not strictly valid in our problem; for we must expect that in the final, steady state attained at any constant traction, there is a fraction of the material not agglomerated. Furthermore, this fraction increases with the traction. In fact, the variation in final viscosity with traction might be explained entirely as the result of variation in the nonagglomerated fraction. However, if this fraction were the only variable factor in the situation, and all agglomerates were of the same density and cohesion, it would be difficult to explain the variation with traction observed in the initial slopes of the $\eta - \tau$ curves. If all agglomerates, both temporary and permanent, had the same cohesion strength, their rate of disruption by the stress would be proportional to the number existing. Hence, in the beginning, when this number is small, their rate of increase would be determined by the agglomerating forces almost uninfluenced by the disrupting forces. The initial increase in viscosity with time would then be independent of the traction, which is contrary to experiment.

Apparently, then, the variation in the initial slopes of the $\eta - \tau$ curves requires the postulate that, under zero stress, agglomerates form with a wide range in cohesive strength but, in the presence of stress, only those agglomerates can form which have a cohesion greater than a critical value which increases with the traction.

It appears from the foregoing arguments that the quantitative theory presented above takes account of the primary factors involved in the process of thixotropic recovery of the latex after stirring. Determination of secondary factors, particularly the amount of nonagglomerated solids in the steady state, will require further experiments which include additional treatments.

ACKNOWLEDGMENT

The experimental data reported in this paper were obtained by W. E. Wolstenholme, now a Lieutenant in the United States Navy.

SUMMARY

A viscometer is described for measuring the viscosity of a liquid immediately after an abrupt reduction of the shearing stress to a very low value. A hollow cylinder on a torsion suspension is immersed in the liquid contained in a narrow annular channel. The inner wall of the channel is rotatable with respect to the outer wall, and by this rotation the liquid is stirred or sheared. After the stirring is stopped, the viscosity is measured by recording photographically the rotation of the hollow cylinder, driven by a nearly constant torque applied through the torsion suspension.

Measurements were made on a commercial compounded rubber latex containing 47.5 per cent of total solids. Immediately after stirring, the latex is a Newtonian liquid with a viscosity of 0.05 poise. Thereafter the viscosity increases at an initial rate and to an ultimate value, both of which decrease as the shearing stress for measuring the viscosity is increased. The steady vis-

cosity is attained approximately in 10 seconds. The observed extremes in steady viscosity were 11 and 0.5 poise, corresponding to the shearing stresses 1.3 and 10.7 dynes per sq. cm.

The experimental data are fitted approximately by theoretical curves based on these assumptions. All aggregates of solid particles are broken up by the stirring. During subsequent thixotropic recovery, loose aggregates are formed which contain considerable trapped water. The rate of aggregation follows Smoluchowski's theory of slow coagulation, but both the coagulation rate constant and the percentage volume of water in the coagulates vary with the applied shearing stress. The relative viscosity of the suspension of aggregates follows an empirical law based on Eilers' data on aqueous suspensions of bitumen spheres.

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THE MEASUREMENT OF THE ADHESION OF UNVULCANIZED RUBBER TO METAL *

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In the processing of unvulcanized rubber and rubberlike materials on mixing mills, calenders, extruders and the like, the adhesion or nonadhesion of the material to metal is well known to be of importance. Similarly in problems of adhesion generally and in particular the bonding of rubber to metal, *e.g.*, by the brass plating technique, an essential criterion for satisfactory adhesion is that the unvulcanized rubber substance shall "wet" the metal completely. Broadly speaking, therefore, there arises a need for a method of measuring the adhesion or rubber or plastic materials in general to metal under various conditions; this adhesion figure gives an indication of the wettability of the metal by the rubber or the rubber/metal interfacial tension. The following method has been developed and may be of value in industries and applications other than that specifically dealt with, namely, unvulcanized rubber. The principle of the method is to observe the angle at which a metal ball rolls off the rubber surface when it is tilted. The metal ball is placed on a plain level surface of the unvulcanized rubber. After a given time the platform on which the rubber lies is tilted slowly and the angle observed at which the ball leaves the rubber and rolls off.

THEORETICAL

The theory can be briefly stated as follows. Consider a sphere resting on a plain level surface of rubber. Depending on the weight of the sphere and the hardness of the rubber, an indentation will be made in the rubber after time t seconds giving an area of contact A. On tilting the rubber surface, the sphere will, at a certain angle which depends on the weight and diameter of the sphere, the amount of indentaion, and the adhesive force of the rubber to the material of the sphere, commence to roll.

Consider a section through the center of the sphere perpendicular to the plane of the rubber and at right angles to the hinge of the tilt. The area of contact is shown in the figure by the sector XY which subtends an angle 2θ at the center. The area A then equals $2\pi r^2(1 - \cos \theta)$.

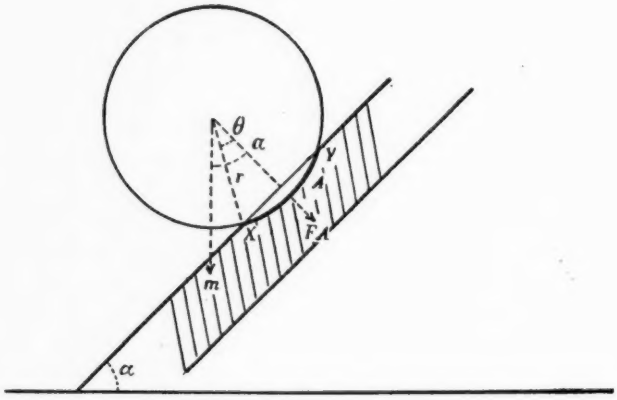
If there is no adhesion between the rubber and the material of the sphere, the angle at which the sphere commences to roll is θ. If there is an adhesive force F per unit area of the contacting surfaces, the sphere commences to roll at an angle α. Considering in this case moments about X, then at the point of rolling the following relation holds:

$$mgr \sin (\alpha - \theta) = FAr \sin \theta$$

* Reprinted from the *Journal of Scientific Instruments*, Vol. 23, No. 10, pages 227–229, October 1946.

where r is the radius of the sphere and m its mass. Substituting for A this equation gives:

$$F = \frac{mg \sin (\alpha - \theta)}{2\pi r^2(1 - \cos \theta) \sin \theta}.$$



Principle of device for the measurement of the adhesion of unvulcanized rubber to metal

r and m can be determined by simple measurement and θ is given by carrying out a measurement under conditions where no adhesion exists between the surfaces. F can then be calculated for various conditions and treatments of the surfaces by determination of α. It is to be noted, however, that the assumption has been made that the tension is uniform over the whole area of contact. Departures from this assumption will occur, and therefore the data given below cannot be considered as absolute.

EXPERIMENTAL

The measurements of the angles θ and α, particularly the former, need to be accurately made, and the apparatus now in use appears satisfactory. It is of simple construction, consisting of a platform, on which is laid the rubber, hinged at one end and raised at the other end by a cord passing over pulleys. To the other end of this cord is attached a weight which falls in a cylinder of oil, diameters and weights being adjusted to give a steady rate of lift of approximately 1 mm. per second. A scale giving the height is read when the ball rolls, and from this reading the angle is calculated.

The variables involved are, in addition to the condition and treatment of the metal and rubber surfaces: (1) weight of ball; (2) diameter of ball; (3) time of contact, *i.e.*, the time that the ball remains on the surface of the rubber in the horizontal position before tilting; (4) temperature.

It is essential to obtain an accurate figure for θ, *i.e.*, for no adhesion of metal to rubber. Several treatments have been tried, of which French chalk seems to be the most satisfactory. Rubber sheets $\frac{1}{16}$–$\frac{1}{4}$ inch in thickness were used.

In practice, it is necessary to choose the ball diameter so that the angle is within the range of the apparatus. Too small a diameter will stick and not roll even at an angle of 45°; too large a diameter leads to inaccuracy since θ is small except in the case of excessively soft materials.

With the apparatus used, having a base of 10 cm., the scale was read to the nearest millimeter, equivalent to $\frac{1}{2}°$, and results were found to be reproducible to within ± 1 mm. in the majority of the experimental work. All tests were carried out at elevated temperatures, 63, 75 and 100° C being used.

EXPERIMENTAL RESULTS

In the following tables some typical results are given which indicate the order of adhesions obtainable and the effect of surface treatments, etc., on the figure.

To obtain θ, in all cases, the rubber surface was dusted with French chalk. Unless otherwise stated, the balls were clean and free from grease or oil, and the rubber surface was smooth (calendered) and thoroughly cleaned with benzene. The details of the balls are given in Table 1 and of the rubber compounds in Table 2.

TABLE 1

DETAILS OF BALLS USED

		Radius (cm.)	Weight (g.)
Steel	A	1.58	129.45
	B	1.12	44.99
	C	0.62	7.99
	D	0.35	1.38
	E	1.22	60.45
	F	1.27	65.68
	G	1.59	130.15
	H	1.90	230.14
Brass	I	1.57	141.83
Aluminum	K	1.57	45.22
Lead	L	1.52	153.56

TABLE 2

DETAILS OF RUBBER COMPOUNDS

Natural rubber	
N1	75 hard (Shore) moulding quality
GR-S (synthetic)	
S1	70 hard (Shore) moulding quality
S2	60 hard (Shore) moulding quality
S3	50 hard (Shore) moulding quality
S4	Calendering quality for fabric topping
S5	Frictioning quality for fabric rubbering
Neoprene	
M1	70 hard (Shore) moulding quality

Where the pressure between rubber and metal has varied in an experiment, due to variation of ball diameter and consequently area of contact, these pressures are given as gm. per sq. cm. (calculated from $m/2\ r^2(1 - \cos\theta)$).

The results given in Table 3, which were obtained with an early form of the apparatus, draw attention to the range of adhesions found. They show also the very marked effect of a treatment of the ball with a solution in aiding the "wetting". The small effect of the size of the ball on the adhesion figure suggests that the theory is fundamentally sound. A further point of interest is the effect of an increase of temperature in making a manifold increase in adhesion, a result in line with practical experience.

TABLE 3

PRELIMINARY EXPERIMENTAL RESULTS ON VARIOUS RUBBERS

Ball diameter and temperature varied. Time of contact, 5 minutes

Compound	Temp. (° C)	F (dynes × 10^3 per sq. cm.) Ball A	Ball B	Ball C	Ball D	F balls painted rubber/resin solution Ball A	Ball B
N1	63	—	350	250	355	740	1050
S1	63	380	350	—	—	855	900
S1	100	—	—	—	—	1150	—
S3	63	620	800	600	—	1240	—
M1	63	135	94	170	132	—	—
M1	100	1200	—	1560	—	—	—

The results in Table 4 are of considerable interest, although the actual adhesions were not all obtainable on account of the softness of the rubber and the size of ball used. Compounds S4 and S5 are designed for calendering and frictioning respectively, *i.e.*, for nonadhesion and adhesion to the steel bowl of the calender, respectively. The very considerable and significant differences in F are clearly brought out. Furthermore, it is customary to apply a casein solution to the bowl to aid adhesion, and in this case ample confirmation is provided that this is efficacious.

TABLE 4

RESULTS ON VARIOUS RUBBERS

Ball No. E; temperature 75° C; time of contact, 2 minutes

Compound	Untreated ball	Ball treated with rubber/resin solution	Ball treated with casein solution	Ball treated with Carbowax
S2	857	1420	—	223
S3	525	> 660	> 660	86
S4	85	302	> 487	—
S5	1040	>1700	>1700	475

The ball size used and other conditions set an upper limit to the adhesion figure recordable.

The effect of rubber solution in increasing adhesion is again shown, and also the effect of Carbowax (a compound containing OH groups, marketed by the Carbide and Carbon Chemical Corporation) in reducing adhesion.

Table 5 calls for little comment, indicating that time of contact is not im-

TABLE 5

VARIATION OF BALL DIAMETER AND TIME OF CONTACT

Rubber compound S2; temperature 75° C

Ball no.	Time of contact (min.)	F (dynes × 10^3 per sq. cm.)	Load (g. per sq. cm.)
F	1	990	650
	2	1070	650
	5	1150	590
G	1	1270	915
	2	1230	825
	5	1090	695
H	1	1550	1460
	2	1750	1280
	5	1610	1130

portant and ball size is important only when the diameter is increased so that the pressure becomes very great.

In all the tables above, the data have been concerned with polished metal surfaces, ordinary polished steel ball-bearings being used. It was of interest to examine balls made of other metal and with surfaces variously roughened. Table 6 shows the results obtained, which indicate that roughening of the sur-

TABLE 6

METAL AND METAL SURFACE

Rubber compound S2; temperature 75° C; time of contact, 2 minutes

	F (dynes $\times 10^3$ per sq. cm.)			
Metal surface	Ball G (steel)	Ball J (brass)	Ball K (aluminum)	Ball L (lead)
Untreated	1540*	>2000	1050	615
Etched	1120	—	—	—
Sand-blasted	545	—	—	—
Zinc plated	1460	940	600	—

* Polished ball-bearing.

face reduces the "wetting". The brass, aluminum and lead balls were unpolished, and this may account for the lower figures. The high figure for brass is due to chemical reaction, which is eliminated by zinc-plating.

SUMMARY

A method is described for measuring the adhesion of metal to unvulcanized rubber and rubberlike materials, which involves the observation of the angle at which a metal ball rolls off the rubber surface when it is tilted. Experimental results are given to confirm the theoretical basis of the method and to illustrate the value of the method in studying the processing characteristics of rubber compounds.

ACKNOWLEDGMENTS

Acknowledgment is made to the laboratories of the John Bull Rubber Company for permission to publish this paper. My thanks are also due to M. W. Smith and (Miss) S. Blair for assistance with the experimental work.

A METHOD FOR PREPARING RUBBER LATEX SPECIMENS FOR THE ELECTRON MICROSCOPE *

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The preparation of natural and synthetic rubber latex specimens for examination with an electron microscope is difficult because the individual particles are easily deformed and, under the usual conditions of specimen preparation, the particles tend to agglomerate. Von Ardenne and Beischer[1] and others[2] used a method which consisted of depositing a drop of highly diluted latex on a collodion film and allowing the drop to dry completely. In some instances the drop was withdrawn again into a glass capillary. It was found that in either case the latex particles were flattened at their areas of contact with the collodion film.

The collodion film method was tried in this laboratory with the same poor results observed by Hendricks, Wildman, and McMurdee[3]. Figure 1 is an electron micrograph of a natural rubber latex particle deposited by evaporating latex diluted 200 to 1 on a collodion film. The film has broken and curled to give a profile view of the particle which is observed to be badly flattened at its area of contact with the film. Figure 2 is a typical electron micrograph of natural rubber latex particles deposited on a collodion film. The blurred outlines of the particles are explained by the effect shown in Figure 1. It was obviously impossible to make good particle-size measurements from micrographs of this type. It was found further that severe aggregation of particles usually took place when a drop of the diluted latex was dried down. The latex particles which were left behind when the drop was removed with a glass capillary usually were not badly agglomerated, but it was felt that there was some possibility that the latex particles might adhere selectively according to size to the collodion film. An attempt was made to reduce the amount of agglomeration by incorporating in the diluting water various amounts of such wetting or dispersing agents as sodium oleate, orvis paste, Aerosol-OT, and ammonium caseinate. None of these materials helped very much in reducing the agglomeration of particles. It was found also in this study that very often the latex particles appeared granular around their edges due to foreign material being swept in during the evaporation of the water and crystallizing out upon the surface of the particle. This effect may also be observed in Figure 1.

The metallic shadow casting technique used by Williams and Wyckoff[4] was not tried in this laboratory. However, it is likely that with this method also the particles would be flattened at their areas of contact with the glass plate. It is probable also that the particles would have a strong tendency to form aggregates.

* Reprinted from the *Journal of Applied Physics*, Vol. 17, No. 8, pages 675–677, August 1946. The present address of the senior author is Department of Physics, University of Minnesota, Minneapolis, Minnesota.

In this laboratory, the following approach to the problem was taken: to disperse the latex in a water solution of a film-forming material and to cast a film from it. In this way the latex particles would be completely surrounded by the material of the film and thus the flattening tendency would be greatly reduced. Polyvinyl alcohol, suggested by R. B. Keller, Jr., proved to be very successful as a water-soluble film forming material. From the standpoint of forming strong clear films, Type *B*, medium viscosity polyvinyl alcohol[5] proved to be best. The method consists of the following operations. Into each of two 10-cc. beakers is placed 1 cc. of 0.5 per cent water solution of polyvinyl alcohol. One drop of the latex is placed in the first beaker and the mixture is stirred vigorously with a glass rod. Approximately two drops of this suspension is transferred to the second beaker and the mixture is stirred vigorously. A 200-mesh specimen screen is first dipped in a 0.5 per cent solution of Aerosol-OT, the excess liquid shaken off and the screen then dipped in the latex-polyvinyl alcohol suspension. The water component of the film adhering to the specimen screen is allowed to evaporate to dryness and the specimen is placed in the microscope.

FIG. 1.—Natural rubber latex particle. Collodion film broken.

Several "kinks" in the technique are to be noted. The specimen screen was held at its edge with a pair of especially prepared tweezers which could be locked shut with a wire catch. The films of polyvinyl alcohol were most

quickly dried in a continuously pumped vacuum desiccator with a small air leak for providing air circulation. The use of the wetting agent Aerosol proved beneficial in promoting the wetting of the wire mesh with the polyvinyl alcohol-latex dispersion. The dilution of the latex had to be varied slightly, of course, depending on the solids content and the particle size. With a little experience a person can estimate the proper dilution of the latex from the turbidity of the final polyvinyl alcohol-latex suspension.

The results obtained by using the polyvinyl alcohol technique are indicated in Figures 3, 4, 5, and 6, which are micrographs obtained with an RCA Type EMU electron microscope. Figure 3 is a micrograph of natural rubber latex. It is to be noted that the outlines of particles are sharp. Figure 4 is a micrograph of natural rubber latex particles in the edge of a broken polyvinyl alcohol

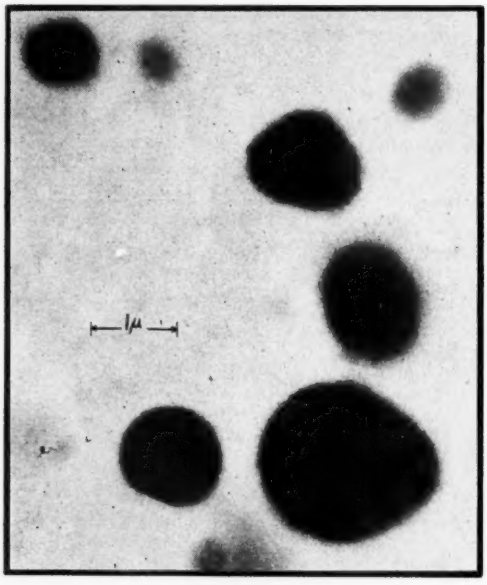

FIG. 2.—Natural rubber latex. Collodion film method.

film which has curled slightly. Figure 5 is similar to Figure 4 except that it is a stereo view. There is no evidence of any flattening of the particles. In general, it has been found that whenever the film is stretched, as around a hole in the film, the latex particles tend to elongate in the direction of stretch as is illustrated in Figures 4 and 5. Figure 6 is a micrograph of a special GR-S type synthetic rubber latex, and it illustrates that synthetic-rubber latex specimens may also be prepared by the polyvinyl alcohol method.

The aggregation of particles is prevented by violent stirring of the polyvinyl alcohol-latex suspension, and fewer aggregates occur than with the drying drop method used with collodion film.

It is a pleasure for the authors to acknowledge the interest shown in this problem by J. H. Dillon and F. W. Stavely. Thanks are due the Firestone Tire and Rubber Company for releasing this paper for publication.

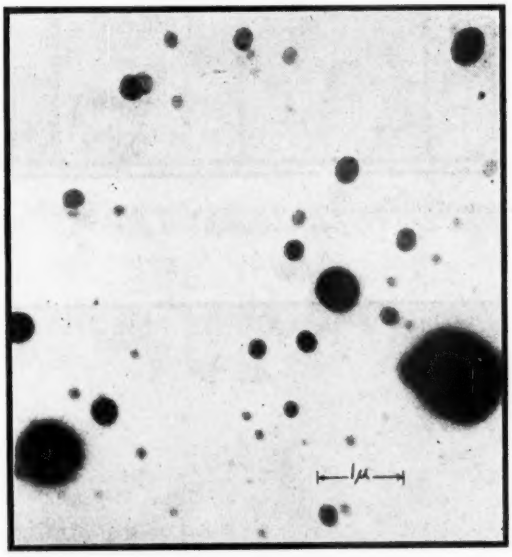

FIG. 3.—Natural rubber latex in polyvinyl. Alcohol film.

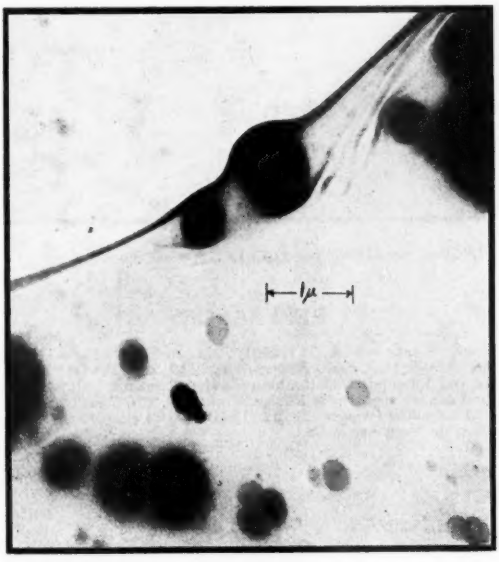

FIG. 4.—Natural rubber latex. Polyvinyl alcohol film broken.

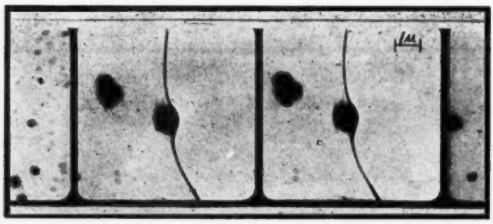

FIG. 5.—Stereo electron micrograph of natural rubber latex imbedded in a broken polyvinyl alcohol film.

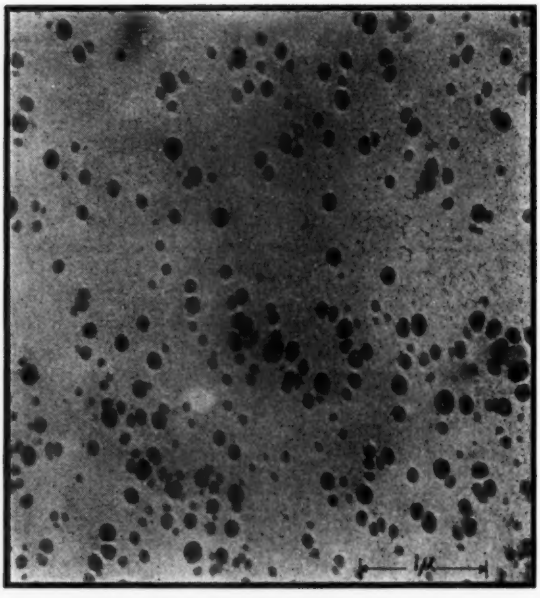

FIG. 6.—GR-S type latex in polyvinyl alcohol film.

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[1] Von Ardenne and Beischer, *Kautschuk* **16**, 55 (1940); RUBBER CHEM. TECH. **14**, 15 (1941).
[2] Hendricks, Wildman and McMurdee, *India Rubber World* **110**, 297 (1944); "Electron Microscope Studies of Rubber Latices and Pigments", Columbian Carbon Research Laboratories, April 1944.
[3] Hendricks, Wildman and McMurdee, *India Rubber World* **110**, 297 (1944).
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[5] Supplied by E. I. du Pont de Nemours & Co.

THEORY OF FILLER REËNFORCEMENT

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A paper on the "Theory of Filler Reënforcement" by Jane M. Dewey was published in the *Journal of Applied Physics*, Vol. 16, No. 1, page 55, January 1945, and was reprinted in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 18, No. 3, pages 605–606, July 1945.

The author has recently published several corrections in the *Journal of Applied Physics*, Vol. 18, No. 1, page 132, January 1947, which RUBBER CHEMISTRY AND TECHNOLOGY takes this opportunity to reprint.

The last line of Equation (3) should read:

$$-\frac{1}{\gamma-1}\left[\frac{\partial P_{\gamma-2}^{|m|}}{\partial\theta}\,i_\theta+\frac{im}{\sin\theta}\,P_{\gamma-2}^{|m|}i_\phi\right]$$

In Equation (5):

$$M=-\tfrac{1}{3}(A+B-2C)P_2(\cos\theta)+\tfrac{1}{12}(A-B)P_2^2(\cos\theta)(e^{2i\phi}+e^{-2i\phi})$$

In Equation (6):

$$\begin{aligned}
b_{-2} &= (3\lambda_1+2\lambda_2-3\lambda_1'-2\lambda_2')(4\lambda_2+3\lambda_1'+2\lambda_2')^{-1}R^3\\
c_{-2} &= -5(3\lambda_1+5\lambda_2)DR^3\\
c_{-4} &= 9(\lambda_1+\lambda_2)DR^5\\
a_1 &= (A+B+C)(\lambda_1+2\lambda_2)(4\lambda_2+3\lambda_1'+2\lambda_2')^{-1}
\end{aligned}$$

RELATIONS BETWEEN THE QUALITY OF LATEX AND ITS CHEMICAL COMPOSITION

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The April 1946 issue of RUBBER CHEMISTRY AND TECHNOLOGY contains, on pages 494–500, a paper entitled "Relations between the quality of latex and its chemical composition", by George Martin.

The author of the paper has called the attention of RUBBER CHEMISTRY AND TECHNOLOGY to errors in three of the tables. Some of these errors were introduced in publication in RUBBER CHEMISTRY AND TECHNOLOGY, others are in the original article in the *Revue Générale du Caoutchouc*.

(1) Table 1, heading "Ammonia (NH_3) content after", third column (2 yrs.).—The first value should be 0.67 instead of 0.76.

(2) Table 1, heading "Stability (no. of thousands of revolutions)", fourth column (3 yrs.).—The first value should be 2 instead of 3.

(3) Table 2. Sample D.—"Cream obtained from recentrifuged latex" should read 'Cream from recentrifuged skim'.

(4) Table 5.—This table should read as follows:

TABLE 5

Sample	Ratio of N_r values (Table 4)	Ratio of N_s values (Table 4)	Relative amounts of serum substances (difference between total solids and dry rubber content)	Ratio of number of revolutions to bring about coagulation with		Ratio of gelling time of latex with sodium fluosilicate	Relative pressure for the same surface concentration of rubber in a Langmuir trough
				sodium fluosilicate	zinc oxide		
A	1.15	2.26	2.3	2.5	2.8	2.5	2.3
B	1.0	1.0	1.0	1.0	1.0	1.0	1.0
D	1.6	1.5	1.7	1.8	1.0	1.6	1.8
E	2.2	2.8	3.3	3.1	3.6	3.1	3.5